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University of Michigan

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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

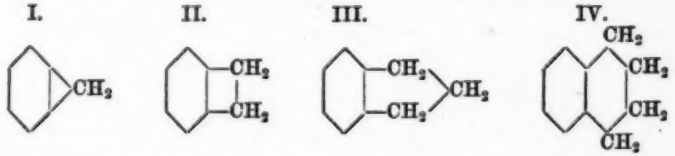
I.—*Synthetical Formation of Closed Carbon-chains in the Aromatic Series.* Part I. *On some Derivatives of Hydrindonaphthene and Tetrahydronaphthalene.*

By W. H. Perkin, Jun., Ph.D.

In previous papers on the "Synthetical Formation of Closed Carbon-chains," I have dealt exclusively with the formation of such chains in the fatty series.

In continuing these researches, it appeared to me that very interesting results might be obtained if substances belonging to the aromatic series were also experimented with. In this way it might be possible to obtain derivatives of the following hydrocarbons:—

I. II. III. IV.



hydrocarbons which would contain, beside the benzene-ring, chains of 3, 4, 5, and 6 carbon-atoms, two atoms of which would invariably be common to both rings.

Although attempts to obtain derivatives of the hydrocarbons I and II have as yet been unsuccessful, substances containing a benzene-ring and a 5-ring (III) and a benzene-ring and a 6-ring (IV) may be synthesised by the following reactions.

Ortho-xylene when treated with 2 mols. of bromine at 125° is converted into ortho-xylylene dibromide, thus:—

$$C_6H_4(CH_3)_2 + 2Br_2 = C_6H_4(CH_2Br)_2 + 2HBr.$$

If now this ortho-xylylene dibromide is digested with ethylic malonate and 2 mols. of sodium ethylate, the following reaction takes place:—

$$C_6H_4(CH_2Br)_2 + Na_2C(COOC_2H_5)_2 = C_6H_4\begin{<}{}^{CH_2}_{CH_2}\end{>}C\begin{<}{}^{COOC_2H_5}_{COOC_2H_5}\end{>} + 2NaBr.$$

The product of this reaction is the ethylic salt of a dicarboxylic acid of a hydrocarbon of the formula—

$$C_6H_4\begin{<}{}^{CH_2}_{CH_2}\end{>}CH_2.$$

The formula represents the dihydride of an unknown hydrocarbon, which stands to indole in the same relation as quinoline does to naphthalene:—

$C_6H_4\begin{<}{}^{CH=CH}_{N=CH}\end{>}$ Quinoline.

$C_6H_4\begin{<}{}^{CH=CH}_{CH=CH}\end{>}$ Naphthalene.

$C_6H_4\begin{<}{}^{CH}_{NH}\end{>}CH$ Indole.

$C_6H_4\begin{<}{}^{CH}_{CH_2}\end{>}CH_2$ Indonaphthene.

and which may therefore be called indonaphthene, in which case the dihydro-derivative would be hydrindonaphthene, and the product of the action of ortho-xylylene dibromide on ethylic malonate ethylic hydrindonaphthenedicarboxylate. This ethereal salt, on hydrolysis, is easily converted into the dicarboxylic acid, which on distillation is resolved into hydrindonaphthenemonocarboxylic acid and carbonic anhydride, thus:—

$$C_6H_4\begin{<}{}^{CH_2}_{CH_2}\end{>}C\begin{<}{}^{COOH}_{COOH}\end{>} = C_6H_4\begin{<}{}^{CH_2}_{CH_2}\end{>}CH\cdot COOH + CO_2.$$

Hydrindonaphthenedicarboxylic acid. — Hydrindonaphthenemonocarboxylic acid.

The attempts to obtain the hydrocarbon direct from its monocarboxylic acid have as yet been without result, but it is hoped that in some indirect way this transformation may still be accomplished.

In continuation of these experiments, I next endeavoured to obtain synthetically derivatives of a hydrocarbon containing two rings, each of 6 carbon-atoms, such as that shown in IV (p. 1), and this, after several failures, was at length accomplished in the following way. Ethylic acetylenetetracarboxylate, when treated with 2 mols. of sodium

ethylate, is converted into a disodium-derivative of the formula $<^{CNa(COOC_2H_5)_2}_{CNa(COOC_2H_5)_2}$, and by digestion with ortho-xylylene dibromide this is easily transformed into the ethylic salt of tetrahydronaphthalenetetracarboxylic acid, thus:—

$$C_6H_4<^{CH_2Br}_{CH_2Br} + <^{CNa(COOC_2H_5)_2}_{CNa(COOC_2H_5)_2} =$$

Ortho-xylylene bromide. Ethylic disodacetylenetetracarboxylate.

$$C_6H_4<^{CH_2\cdot C(COOC_2H_5)_2}_{CH_2\cdot C(COOC_2H_5)_2} + 2NaBr.$$

Ethylic tetrahydronaphthalenetetracarboxylate.

If this ethereal salt is treated with alcoholic potash, hydrolysis sets in, but at the same time 2 mols. of CO_2 are removed, and the potassium salt of tetrahydronaphthalenedicarboxylate is formed, thus:—

$$C_6H_4<^{CH_2\cdot C(COOC_2H_5)_2}_{CH_2\cdot C(COOC_2H_5)_2} + 6KOH =$$

$$C_6H_4<^{CH_2\cdot CH\cdot COOK}_{CH_2\cdot CH\cdot COOK} + 4C_2H_6O + 2K_2CO_3.$$

Potassic tetrahydronaphthalenedicarboxylate.

On acidifying the aqueous solution of this salt with dilute sulphuric acid, tetrahydronaphthalenedicarboxylic acid is obtained. This acid, being an orthodicarboxylic acid similar to phthalic acid, is on heating easily converted into its anhydride and water, thus:—

$$C_6H_4<^{CH_2\cdot CH\cdot COOH}_{CH_2\cdot CH\cdot COOH} = C_6H_4<^{CH_2\cdot CH\cdot CO}_{CH_2\cdot CH\cdot CO}>O + H_2O.$$

But the most interesting decomposition of this acid is that which it undergoes when its silver salt is distilled. Under these circumstances, it is completely decomposed into the anhydride of the acid and naphthalene, thus:—

$$2C_6H_4<^{CH_2\cdot CH\cdot COOAg}_{CH_2\cdot CH\cdot COOAg} = C_6H_4<^{CH=CH}_{CH=CH} +$$

Naphthalene.

$$C_6H_4<^{CH_2\cdot CH\cdot CO}_{CH_2\cdot CH\cdot CO}>O + 4Ag + 2CO_2 + H_2O$$

Now ethylic acetylenetetracarboxylate is formed from 2 mols. of ethylic malonate by the abstraction of two atoms of hydrogen. It, therefore, follows that one should obtain the same result as the above, if ortho-xylylene dibromide were combined first with 2 mols. of ethyl malonate, and the two atoms of hydrogen were then removed. For this purpose two molecular proportions of the monosodium-derivative of ethylic malonate were treated with one molecular proportion of ortho-xylylene dibromide in the expectation of realising the following reaction:—

$$C_6H_4(CH_2Br)_2 + 2NaHC(COOC_2H_5)_2 = C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2 + 2NaBr,$$

but on examining the product it was found that ethylic hydrindo-naphthenedicarboxylate had been formed, a result which can only be explained by supposing that an interchange of sodium-atoms takes place between the 2 mols. of ethylic malonate, much in the same way as in the formation of ethylic methyldehydrohexonecarboxylate from 2 mols. of the monosodium-derivatives of ethylic acetoacetate, and 1 mol. of trimethylene bromide (Trans., 1887, 703), thus:—

$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + 2NaHC(COOC_2H_5)_2 = C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 + 2NaBr.$$

This difficulty can be got over, however, by substituting in the above reaction the sodium-derivative of ethylic monochlormalonate for that of ethylic malonate.

In this case, the following reaction takes place:—

$$C_6H_4(CH_2Br)_2 + 2NaClC(COOC_2H_5)_2 = C_6H_4[CH_2\cdot ClC(COOC_2H_5)_2]_2 + 2NaBr,$$

Ethylic ortho-xylylenedichlordimalonate.

ethylic ortho-xylylenedichlordimalonate being formed.

If this ethereal salt is reduced with zinc and acetic acid, the two chlorine-atoms become displaced by hydrogen and ethylic ortho-xylylenedimalonate is formed, thus:—

$$C_6H_4[CH_2\cdot ClC(COOC_2H_5)_2]_2 + 4H = C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2 + 2HCl.$$

Ethylic ortho-xylylenedimalonate.

If this substance be now treated with two molecular proportions of sodic ethylate, the two hydrogen-atoms of the CH groups will be displaced by sodium, forming a disodium-derivative, which when mixed

with an ethereal solution of iodine is converted quantitatively into ethylic tetrahydronaphthalenetetracarboxylate, thus:—

$$C_6H_4<\begin{matrix}CH_2\cdot CNa(COOC_2H_5)_2\\ CH_2\cdot CNa(COOC_2H_5)_2\end{matrix} + I_2 =$$

$$C_6H_4<\begin{matrix}CH_2\cdot C(COOC_2H_5)_2\\ |\\ CH_2\cdot C(COOC_2H_5)_2\end{matrix} + 2NaI.$$

Orthoxylylene Dibromide, $C_6H_4<\begin{matrix}CH_2Br\ (1)\\ CH_2Br\ (2)\end{matrix}$.

Ortho-xylylene dibromide is best prepared in the following way:—·50 grams of pure ortho-xylene are placed in a large tubulated retort connected with a long reflux condenser, and after being heated carefully to 125—130° by means of an oil-bath, the calculated quantity of bromine (160 grams) is allowed to drop in very slowly through a dropping funnel. Torrents of hydrogen bromide are evolved, but the liquid should remain almost colourless till the end of the operation, when it usually assumes a slightly brownish tint. It is necessary to add the bromine very slowly, otherwise the reaction is apt to become violent, in which case, if the condensing apparatus is not very good, small quantities of ortho-xylene get carried away by the hydrogen bromide vapours.

It is also important to keep the temperature of the oil-bath between 125° and 130° (the temperature 150—155°, first given in the *Berichte*, **17**, 123, is too high), and then the resulting product is almost colourless. As soon as the reaction is over, the resulting crude dibromide is poured out into a small beaker, covered up with a watch-glass, and allowed to stand for 24 hours, when the whole solidifies to a cake of crystals. These are purified from oily mother-liquor by spreading out on a porous plate, and are thus obtained almost colourless and sufficiently pure for ordinary purposes. If the reaction has been successful, the yield of this product should be about 85—90 grams.

In order to obtain pure ortho-xylylene dibromide these crystals are washed with chloroform and then recrystallised from this solvent. An analysis gave the following numbers:—

0·2122 gram substance gave 0·3017 gram AgBr.

	Theory. $C_6H_4(CH_2Br)_2$.	Found.
Br.....	60·60 per cent.	60·50 per cent.

Ortho-xylylene dibromide melts at 93°, and dissolves in about five parts of ether. It crystallises from chloroform or ether in magnifi-

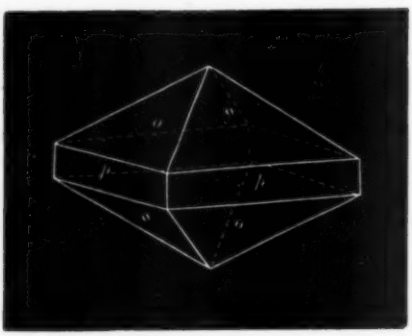
cent, large, glittering crystals, which Professor Haushofer was kind enough to examine crystallographically. He gave me the following account of his experiments:—

Crystalline System: Rhombic.

$a : b : c = 0{\cdot}8581 : 1 : 0{\cdot}5014.$

Well developed crystals of the combination $P . \infty P = (111)(110)$, with tolerably smooth and even surfaces but cloudy. The prismatic faces (p) very subordinate and often reduced to narrow streaks.

	Measured.		Calculated.		
$p : p = (110)(1\bar{1}0) =$	*98	44′	—	—	(brachydiagonal prismatic edge).
$p : p = (110)(\bar{1}10) =$	81	16	81°	16′	(macrodiagonal).
$p : o = (110)(111) =$	*127	36	—	—	
$o : o = (111)(\bar{1}11) =$	125	appr.	124	50	(macrodiagonal polar edge).
$o : o = (111)(1\bar{1}1) =$	132	27	133	10	(brachydiagonal).



Before proceeding further, it was necessary to prove that the bromine-atoms in this product were situated one in each methyl group. This was done in the following way: 5 grams of the pure substance was mixed with an excess of sodium carbonate solution, and boiled with a reflux condenser till the oily drops had entirely disappeared, which was the case in about three hours. The solution was then filtered from a small quantity of an insoluble substance, and extracted twice with pure ether. The ethereal solution after drying, filtering, and evaporating, deposited a colourless syrup, which, on standing, solidified almost completely to a mass of crystals, melting at about 66—72°. To purify these, the crude mass was spread out on a porous plate, recrystallised once from ether, and analysed:—

0·1102 gram substance gave 0·0744 gram H_2O and 0·2792 gram CO_2.

	Theory. $C_6H_4(CH_2\cdot OH)_2$.	Found.
C	69·56 per cent.	69·11 per cent.
H	7·25 „	7·50 „
O	23·19 „	23·39 „

This substance now melted at about 62—64°, and proved to be identical with the phthalyl alcohol first obtained by Hessert (*Ber.*, **12**, 646). When mixed with concentrated sulphuric acid, the dark-red solution described by him was first formed; but this colour in a short time disappeared owing to the substance being completely decomposed. The constitution of this alcohol was definitely proved by the fact that when oxidised either with permanganate or with chromic mixture, it yielded phthalic acid.

In preparing and experimenting with ortho-xylylene dibromide, it is necessary to work either in a very good draught closet or, better still in the open air, as the vapours of this substance have a most irritating and painful effect on the skin and eyes.

Hydrindonaphthenedicarboxylic Acid, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C(COOH)_2$.

In preparing this acid, the following method has been found to give the best results:—

0·9 gram of sodium is dissolved in 10 grams of absolute alcohol, and the solution, while still warm, is mixed with 40 c.c. of pure dry ether. To this solution, 3 grams of ethyl malonate dissolved in 10 c.c. of ether and 5 grams of ortho-xylene dibromide dissolved in 30 or 40 c.c. of ether are rapidly added, and the whole allowed to remain for about three hours at the ordinary temperature. Shortly after mixing, a thick voluminous precipitate of the sodium-derivative of ethyl malonate separates out; but this soon gives place to a heavy, sandy precipitate, which consists not only of sodium bromide, but also contains an organic sodium compound—possibly an intermediate substance of the formula $CH_2Br\cdot C_6H_4\cdot CH_2\cdot CNa(COOC_2H_5)_2$.

After standing for three hours, the ethereal solution is separated* from the precipitate by filtration, and evaporated. The residue from this, as well as the precipitate, are dissolved in a little pure alcohol and digested with an excess of alcoholic potash, using a reflux condenser until, on the addition of water, no more oil is precipitated; this usually takes place in about 10 minutes. After distilling off the alcohol, the residue is dissolved in a considerable quantity of water, gently evaporated on a water-bath to get rid of the last traces of

* If the ether be distilled off without separating the solution from the precipitate, vigorous bumping usually sets in.

alcohol, filtered if necessary, and acidified with dilute sulphuric acid; this often causes the precipitation of a small quantity of a resinous substance, which must be filtered off before proceeding further. The clear solution is now extracted several times with pure ether, the ethereal solution dried over a little calcic chloride, and evaporated. In this way, hydrindonaphthenedicarboxylic acid is obtained as an almost colourless crystalline mass which, after removal of traces of oil by spreading it on a porous plate and recrystallising from water, is easily obtained in a pure state. The analysis gave the following numbers:—

0·1460 gram substance gave 0·0662 gram H_2O and 0·3411 gram CO_2.

	Theory. $C_{11}H_{10}O_4$.	Found.
C	64·07 per cent.	63·72 per cent.
H	4·86 „	5·03 „
O	31·07 „	31·25 „

Hydrindonaphthenedicarboxylic acid crystallises from water in rhombic plates which melt at 199°, and, at a slightly higher temperature, decompose rapidly into carbonic anhydride and hydrindonaphthenemonocarboxylic acid. The dicarboxylic acid is fairly easily soluble in hot water, alcohol, and ether, but much less so in cold water.

The silver salt was prepared by adding nitrate of silver to a warm neutral solution of the ammonium salt; it is obtained as a white, amorphous precipitate, which becomes crystalline on standing. After collecting, washing with a little water, and drying, first on a porous plate and then at 100°, it was analysed with the following results:—

I. 0·1670 gram substance gave 0·0305 gram H_2O, 0·1920 gram CO_2, and 0·0868 gram silver.

II. 0·1900 gram substance gave 0·0975 gram silver.

	Theory. $C_{11}H_8O_4Ag_2$.	Found. I.	Found. II.
C	31·43 per cent.	31·35	—
H	1·90 „	2·03	—
Ag	51·42 „	51·97	51·32
O	15·24 „	14·65	—

Hydrindonaphthenemonocarboxylic Acid, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot COOH$.

In order to prepare this acid, the dicarboxylic acid (1 gram) is rapidly distilled from a very small retort over a naked Bunsen flame.

The acid first melts and decomposes with evolution of carbonic anhydride; on raising the temperature, an almost colourless oil distils over, which crystallises at once on the cool sides of the neck of the retort. No residue is left if the distillation is conducted rapidly. Hydrindonaphthenemonocarboxylic acid obtained in this way is almost pure; for the analysis—which was made with lead chromate owing to the difficulty in burning the substance—it was once recrystallised from water:—

I. 0·1642 gram substance gave 0·0945 gram H_2O and 0·4451 gram CO_2.

II. Details of this analysis are missing.

	Theory. $C_{10}H_{10}O_2$.	Found. I.	Found. II.
C	74·07 per cent.	73·91	73·67
H	6·17 „	6·39	6·70
O	19·75 „	19·70	19·63

Some interesting experiments with hydrindonaphthenemonocarboxylic acid have been made by E. Scherks (*Ber.*, **18**, 378).

Hydrindonaphthenemonocarboxylic acid is formed directly by the action of ortho-xylylene dibromide on the sodium-derivative of ethylic acetoacetate and subsequent hydrolysis with alcoholic potash:—

(1.) $C_6H_4<\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + CH_2<\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix} + Na_2 =$

$$2NaBr + C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix}.$$

(2.) $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix} + 2KOH = CH_3\cdot COOK +$

$$C_2H_5\cdot OH + C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot COOK.$$

The yield, however, in this case is considerably less than that obtained when ethyl malonate is used.

When hydrindonaphthenemonocarboxylic acid is oxidised with alkaline permanganate, it is converted into the orthocarboxylic acid of phenylglyoxylic acid (Scherks, *loc. cit.*)—

$$\begin{matrix}C_6H_4\cdot CH_2\\|\quad\quad|\\CH_2\cdot CH\cdot COOH\end{matrix} + 7O = \begin{matrix}C_6H_4\cdot COOH\\|\\CO\cdot COOH\end{matrix} + CO_2 + 2H_2O.$$

This acid, on reduction, yields phthalidecarboxylic acid:—

$$\begin{matrix}C_6H_4\cdot COOH\\|\\CO\cdot COOH\end{matrix} + H_2 = \begin{matrix}C_6H_4\cdot COOH\\|\\CH(OH)\cdot COOH\end{matrix} = \begin{matrix}C_6H_4\cdot CO\\|\quad\quad|\\COOH\cdot CH-O\end{matrix} + H_2O,$$

an acid which, when heated to temperatures above 180°, is converted into phthalide and carbonic anhydride, thus :—

$$\begin{array}{l} C_6H_4\cdot CO \\ | \quad | \\ COOH\cdot CH-O \end{array} = \begin{array}{l} C_6H_4\cdot CO \\ | \quad | \\ CH_2-O \end{array} + CO_2.$$

As is seen at a glance, this interesting decomposition of hydrindonaphthenemonocarboxylic acid on oxidation goes far to prove the formula ascribed to the acid in this paper.

Hydrindonaphthenemonocarboxylic acid melts at 130°, and, when strongly heated, distils without decomposition.

It is sparingly soluble in cold water, but dissolves in about 120 parts of boiling water. If this hot solution is allowed to cool slowly, it becomes first quite milky, and then deposits the acid in slender, colourless needles. The silver salt was prepared from the ammonium salt in the usual way. It is a bulky white precipitate, almost insoluble in cold, but apparently slightly soluble in hot water. For the analysis, it was well washed with water, and dried over sulphuric acid in a vacuum.

0·1186 gram substance gave 0·0476 gram silver.

	Theory. $C_{10}H_9O_2Ag$.	Found.
Ag.....	40·15 per cent.	40·13 per cent.

Action of Benzyl Chloride on the Sodium-derivative of Ethylic Acetylenetetracarbozylate.

Benzylsuccinic Acid, $\begin{array}{l} C_6H_5\cdot CH_2\cdot CH\cdot COOH \\ | \\ CH_2\cdot COOH \end{array}$.

Before using ethylic acetylenetetracarboxylate for the synthesis of tetrahydronaphthalene-derivatives it was necessary to prove that the former could form a disodium-derivative when treated with sodic ethylate. To ascertain this, a quantity of the ethylic salt was dissolved in alcohol and mixed with the calculated quantity of sodic ethylate (2 mols.), and the resulting clear solution agitated with three times its volume of pure dry ether. This caused the precipitation of the disodium-derivative as a heavy white mass, which was collected and well washed by means of a vacuum pump, first with a mixture of alcohol and ether, and lastly with pure ether. The product was dried over sulphuric acid in a vacuum, and analysed with the following result :—

0·2323 gram substance gave 0·0889 gram Na_2SO_4.

	Theory. $C_{14}H_{20}Na_2O_4$.	Found.
Na.....	12·71 per cent.	12·38 per cent.

The action of benzyl chloride on this sodium compound was next tried. 2 grams of the latter were mixed with a little alcohol and heated in a sealed tube with excess of benzyl chloride for a short time at 150°. The product was diluted with water, the oil thus precipitated extracted with ether, and the ethereal solution washed, dried over calcic chloride, and evaporated; the colourless oil which remained was then hydrolysed by boiling it with excess of alcoholic potash. The product was dissolved in water, evaporated on a water-bath until all the alcohol had been driven off, acidified with dilute sulphuric acid, and extracted about 20 times with pure ether. On distilling off the ether, a slightly brownish syrup remained behind which, when heated, gave off carbonic anhydride, and was converted into a brownish oily mass; this on standing crystallised for the most part. The crystals were purified by washing with chloroform, in which they are sparingly soluble, and then analysed with the following results :—

	Theory. $C_{11}H_{12}O_4$.	Found.
C.....	63·46 per cent.	63·14 per cent.
H.....	5·77 „	5·84 „
O.....	30·77 „	31·02 „

This substance was therefore benzylsuccinic acid.

I did not examine this acid further, as the only reason for preparing it was to ascertain whether the sodium-atoms of the disodium-derivative of ethylic acetylenetetracarboxylate could be displaced by organic radicles.

This reaction has, since the first publication of these results (*Ber.*, **17**, 449), been carefully studied by Bischoff and Rach (*Ber.*, **17**, 2783).

Tetrahydronaphthalenedicarboxylic Acid ($\beta\beta$), $C_6H_4\begin{<}\begin{matrix}CH_2\cdot CH\cdot COOH\\ CH_2\cdot CH\cdot COOH\end{matrix}$.

In using ortho-xylylene dibromide for the following synthetical experiments, the sparing solubility of the substance in alcohol was at first a source of trouble; it was, however, soon found that this could be got over by first dissolving the bromide in ether, adding the alcohol, and then distilling off the ether, when a supersaturated solution remains which does not crystallise for some time. In preparing tetrahydronaphthalenedicarboxylic acid, the following method was found to give good results :—

A mixture of 1 molecular proportion of ortho-xylylene dibromide dissolved in 5 parts of alcohol, 1 molecular proportion of ethylic acetylenetetracarboxylate in 5 parts of alcohol, and 2 atomic proportions of sodium in 15 parts of alcohol were heated together in a sealed tube for six hours at 130°; it was found that sodium bromide separated, and on opening the tube a slight pressure was observable. The contents were emptied into a flask, mixed with a strong solution of alcoholic potash (containing 8 mols. KHO), and allowed to stand at the ordinary temperature for 12 hours; at the end of that time, the mass was gently warmed on a water-bath until a sample taken out dissolved in water without the precipitation of oily drops. The whole was then mixed with water, evaporated on a water-bath almost to dryness, again dissolved in a small quantity of water, acidified with dilute sulphuric acid, and the solution filtered from a few particles of resinous matter which had separated. The clear liquid was now extracted 10 times with pure ether (free from alcohol), the ethereal solution dried over calcic chloride, filtered and evaporated, when an almost colourless syrup was obtained consisting probably for the most part of tetrahydronaphthalenetetracarboxylic acid, $C_6H_4\begin{<}\begin{matrix}CH_2\cdot C(COOH)_2\\ |\\ CH_2\cdot C(COOH)_2\end{matrix}$.

This was not further examined, but directly transferred to a small flask and heated in an oil-bath gradually to 185°. During this operation, a considerable quantity of carbonic anhydride and aqueous vapour was given off, and a thick oily residue was left which, on cooling, solidified to a mass of crystals. These were pounded up, agitated with a little dry ether, filtered, and well washed with ether; they were thus obtained as a white crystalline powder, which on examination proved to be the anhydride of tetrahydronaphthalenedicarboxylic acid.

The formation of this anhydride from tetrahydronaphthalenetetracarboxylic acid is represented in the following equation:—

$$C_6H_4\begin{<}\begin{matrix}CH_2\cdot C(COOH)_2\\ |\\ CH_2\cdot C(COOH)_2\end{matrix} = C_6H_4\begin{<}\begin{matrix}CH_2\cdot CH\cdot CO\\ |\\ CH_2\cdot CH\cdot CO\end{matrix}\!\!>O + 2CO_2 + H_2O.$$

This product after recrystallising from ether gave the following numbers on analysis:—

0·2000 gram substance gave 0·5214 gram CO_2 and 0·0882 H_2O.

	Theory. $C_{12}H_{10}O_3$.	Found.
C	71·28 per cent.	71·10 per cent.
H	4·95 ,,	4·90 ,,
O	23·76 ,,	24·00 ,,

The anhydride is sparingly soluble in ether, but more readily so in alcohol and chloroform. On slowly evaporating its solution in warm ether, it crystallises in large four-sided prisms which melt at 184°. The yield obtained was 70 per cent. of the theoretical.

If the vapour of this anhydride is passed through a red-hot tube, a considerable quantity of naphthalene is formed, a decomposition which is referred to in the introduction. The naphthalene thus obtained was not analysed, but was sharply characterised by its melting point (79°), its odour, and by converting it into the characteristic picric acid compound; as there could be no doubt of its identity with ordinary naphthalene, it was not thought necessary to prepare enough for analysis, which would have entailed the loss of a large quantity of valuable material.

The anhydride of tetrahydronaphthalenedicarboxylic acid is insoluble in cold water, but is slowly altered by boiling water with formation of the acid. In order to obtain the acid, the anhydride was warmed with a little sodic hydrate solution, in which it dissolves fairly easily, the solution cooled and acidified with dilute sulphuric acid. On standing, the dicarboxylic acid separates as a white crystalline powder, which when examined under the microscope is found to consist of small rhombic plates. Analysis gave the following results:—

0·1740 gram substance gave 0·4154 gram CO_2 and 0·0877 gram H_2O.

	Theory. $C_{12}H_{12}O_4$.	Found.
C	65·45 per cent.	65·10 per cent.
H	5·46 „	5·60 „
O	29·09 „	29·30 „

Tetrahydronaphthalenedicarboxylic acid is sparingly soluble in cold, but more easily so in hot water. It dissolves freely in chloroform, alcohol, and acetone. The pure acid melts at 199°, being at the same time converted into its anhydride; this is clearly shown by the fact that if the substance which has been used for determining the melting point of the acid, be allowed to cool, and then remelted, it will now melt at 184°, which is the melting point of the anhydride.

The silver salt of this acid is prepared by adding silver nitrate to a neutral solution of the ammonium salt, and is thus obtained as a white amorphous precipitate, which on standing becomes crystalline. It is rapidly discoloured by the action of light, and should therefore be prepared in the dark. Analysis gave the following result:—

0·1665 gram substance gave 0·2042 gram CO_2, 0·0338 gram H_2O, and 0·0825 gram Ag.

	Theory. $C_{12}H_{10}O_4Ag_2$.	Found.
C	33·18 per cent.	33·44 per cent.
H	2·30 „	2·26 „
Ag	49·77 „	49·55 „
O	14·75 „	14·75 „

If this silver salt is gently heated in a test-tube, it is easily decomposed, and on further heating a mixture of naphthalene and the anhydride of tetrahydronaphthalenedicarboxylic acid distils and condenses on the cooler part of the tube; there is no charring.

Ethylic Ortho-xylylenedichlorodimalonate,
$C_6H_4[CH_2{\cdot}CCl{:}(COOC_2H_5)_2]_2$.

In order to prepare this substance, pure ethylic monochloromalonate (2 mols.) is dissolved in the calculated quantity of sodic ethylate (2 mols.), the mixture diluted with its own volume of pure dry ether, and then slowly added to an ethereal solution of ortho-xylylene dibromide (1 mol.). The whole is now gently warmed on a water-bath for about three hours, at the end of which time the reaction is complete.

In order to isolate the product, water is added, the ethereal solution separated, well washed with water, dried over calcic chloride, and the ether distilled off, when a thick, almost colourless, oil remains consisting of nearly pure ethylic ortho-xylylenedichlorodimalonate. After the substance had been allowed to stand for some days over sulphuric acid in a vacuum, a chlorine determination was made with the following result:—

	Theory. $C_{22}H_{28}Cl_2O_8$.	Found.
Cl	14·49 per cent.	13·9 per cent.

Ethylic ortho-xylylenedichlorodimalonate is a thick, almost colourless syrup, which on long standing solidifies to large, colourless crystals. It cannot be purified by distillation even in a vacuum, but when prepared by the above method it is pure enough for all further experiments.

Orthophenylenediacrylic Acid, $C_6H_4(CH : CH{\cdot}COOH)_2$.

The potassium salt of this acid is formed when ethylic ortho-xylylenedichlorodimalonate is boiled with alcoholic potash, thus:—

$$C_6H_4[CH_2{\cdot}CCl(COOC_2H_5)_2]_2 + 8KOH = C_6H_4(CH : CH{\cdot}COOK)_2 + 4C_2H_5{\cdot}OH + 2KCl + 2K_2CO_3 + 2H_2O.$$

This decomposition is carried out in the following way :—

Ethylic ortho-xylylenedichlorodimalonate is dissolved in a little alcohol, the solution mixed with excess of concentrated alcoholic potash (10 mols. of KOH), and heated to boiling on a water-bath for four hours in a flask connected with a reflux condenser. During the operation, a quantity of potassic chloride and carbonate separates out as a heavy sandy precipitate, which sometimes causes bumping to such an extent that it is necessary to remove it by filtration before the hydrolysis can be proceeded with. As soon as this is completed, the alcohol is distilled off as far as possible, the residue dissolved in water, evaporated on a water-bath till all the alcohol has been driven off, and the solution filtered and acidified with dilute sulphuric acid. This causes the new acid to be precipitated in the form of light yellow flocks; when collected, well washed with water and dried, it is nearly pure. For analysis, the substance was washed with acetone, redissolved in dilute carbonate of soda, the solution boiled for some time with animal charcoal, filtered, and the acid reprecipitated with dilute sulphuric acid. In this way it was obtained as an almost colourless flocculent mass, which after very careful washing and drying gave the following numbers on analysis :—

I. 0·1365 gram substance gave 0·3306 gram CO_2 and 0·0605 gram H_2O.

II. 0·1612 gram substance gave 0·3900 gram CO_2 and 0·0723 gram H_2O.

	Theory. $C_{12}H_{10}O_4$.	Found. I.	Found. II.
C	66·05 p. c.	66·05	65·98 p. c.
H	4·59 „	4·96	4·98 „
O	29·36 „	28·89	29·04 „

Orthophenylenediacrylic acid is very sparingly soluble in toluene, alcohol, benzene, chloroform, and ether, slightly more soluble in acetone and water. It can with difficulty be recrystallised from acetone, but as it is so very pure when prepared as above, this is not necessary.

Orthophenylenediacrylic acid melts above 300°, and when heated in small quantities in a test-tube it sublimes, but with considerable decomposition. In order to prepare the silver salt, the pure acid was dissolved in dilute ammonia, carefully neutralised with dilute nitric acid, and precipitated with nitrate of silver. In this way an almost colourless insoluble silver salt was obtained, which after well washing and drying over sulphuric acid in a vacuum gave the following result on analysis :—

0·2982 gram substance gave 0·1477 gram Ag.

	Theory. $C_{12}H_8O_4Ag_2$.	Found.
Ag.....	50·00 per cent.	49·54 per cent.

If the solution of orthophenylenediacrylic acid in dilute sodic hydrate, be treated with benzene and potassic permanganate (according to the method described by Einhorn for the preparation of orthonitrobenzoic aldehyde, *Ber.*, **17**, 119), an oil is obtained which has all the properties of an aldehyde, and which, as it gives phthalic acid on oxidation, is possibly phthalic aldehyde.

Ethylic Ortho-xylylenedimalonate, $C_6H_4[CH_2{\cdot}CH : (COOC_2H_5)_2]_2$.

This compound is formed, as was mentioned in the introduction, by the action of reducing agents on ethylic ortho-xylylenedichlorodimalonate. In preparing it, about 10—15 grams of the latter are dissolved in 80—100 c.c. of glacial acetic acid, and then zinc-dust is slowly added in small quantities at a time, the whole being vigorously shaken after each addition. It is important to add only small quantities of zinc-dust at a time, otherwise it is apt to cake together at the bottom of the flask, and thus be of little use. During the reaction, a considerable rise of temperature takes place, and after a time the liquid becomes quite thick from separation of zincic acetate. When it has reached this stage, a little water is added, and the whole warmed on a water-bath for about half an hour. The supernatant liquid is now poured off from the undissolved zinc into about three times its volume of water, and the oil thus precipitated extracted three or four times with ether. The residual zinc is also extracted four or five times with ether, the two ethereal solutions mixed together, and freed from acetic acid by washing first with water and then with dilute carbonate of soda solution. Lastly, the ethereal extract is dried over potassic carbonate, and the ether distilled off, when a colourless oil remains, consisting of nearly pure ethylic ortho-xylylenedimalonate.

In preparing this substance, it often happens that the product is found still to contain chlorine; if this is the case, it is necessary to repeat the reduction until all the chlorine has been removed.

Ethylic ortho-xylylenedimalonate cannot be purified by distillation even in a vacuum, and in order to prepare it for analysis, advantage had to be taken of the sodium-derivative which it forms. A weighed quantity of the oil (1 mol.) when dissolved in ether and mixed with an ethereal solution of sodic ethylate (2 mols.) is converted into a disodium-derivative, which separates in white flocks, whereas any

impurities present remain in solution, and can be removed by collecting the precipitate and washing it with ether. If the sodium-derivative thus obtained be mixed with dilute sulphuric acid, it is instantly decomposed, and pure ethylic ortho-xylylenedimalonate is set free. This after extraction with ether and washing with sodic carbonate is obtained as a thick, colourless oil. In order to be certain of the purity of the sample analysed, this operation was repeated twice, and with the product thus obtained, the following analysis was made :—

0·1365 gram substance gave 0·3140 gram CO_2 and 0·0884 gram H_2O.

	Theory. $C_{22}H_{30}O_8$.	Found.
C	62·56 per cent.	62·73 per cent.
H	7·11 „	7·19 „
O	30·33 „	30·18 „

Ethylic ortho-xylylenedimalonate thus prepared is a thick colourless syrup, insoluble in water, but easily soluble in alcohol, ether, and most of the usual solvents.

Its most important property is that when mixed with sodic ethylate it forms a disodium-derivative, and before proceeding with this research it appeared necessary to prove the constitution of this compound by analysis.

To prepare as pure a sample as possible, pure ethylic ortho-xylylenedimalonate was dissolved in pure dry ether and mixed with the calculated quantity of an ethereal solution of sodic ethylate ; after the precipitation was complete, the sodium-derivative was collected on a filter-pump as rapidly as possible, washed several times with ether, and then spread out on a porous plate, and transferred to a vacuum desiccator. The following is the result of analysis :—

	Theory. $C_{22}H_{28}O_8Na_2$.	Found.
Na	9·9 per cent.	9·12 per cent.

This compound is a colourless, hygroscopic mass, and for this reason the numbers obtained were rather lower than those required by theory. When mixed with acids, it is instantly decomposed with regeneration of ethylic ortho-xylylenedimalonate.

In experimenting further with the latter substance, it was not purified by conversion into the disodium-derivative and reprecipitation as described above, as this is always attended with great loss of substance, probably owing to partial hydrolysis. It was found that the crude product of the reduction of ethylic ortho-xylylenedichloro-

malonate was sufficiently pure to render this process of purification unnecessary.

Orthophenylenedipropionic Acid, $C_6H_4(CH_2{\cdot}CH_2{\cdot}COOH)_2$.

This acid is obtained by the hydrolysis of ethylic ortho-xylylenedimalonate with alcoholic potash, thus :—

$$C_6H_4[CH_2{\cdot}CH(COOC_2H_5)_2]_2 + 6KOH = C_6H_4(CH_2{\cdot}CH_2{\cdot}COOK)_2 + 2K_2CO_3 + 4C_2H_5{\cdot}OH.$$

In preparing it, ethylic ortho-xylylenedimalonate was boiled with a considerable excess of concentrated alcoholic potash for some hours on a sand-bath until hydrolysis was complete. Water was then added, the solution evaporated on a water-bath until all the alcohol had been driven off, filtered and acidified with dilute sulphuric acid; this precipitates the new acid as a yellowish-white, flocculent mass which, after collecting, drying, and washing with hot chloroform, is easily obtained pure by recrystallising once or twice from water. On analysis, the following results were obtained :—

I. 0·1357 gram substance gave 0·3237 gram CO_2 and 0·0794 gram H_2O.

II. 0·1811 gram substance gave 0·4358 gram CO_2 and 0·1068 gram H_2O.

	Theory. $C_{12}H_{14}O_4$.	Found. I.	Found. II.
C	64·86 p. c.	65·05	65·00 p. c.
H	6·31 „	6·50	6·55 „
O	28·82 „	28·45	28·45 „

Orthophenylenedipropionic acid crystallises from water in small, colourless, microscopic needles, which melt not very sharply at about 160—162°. The silver salt which was prepared from the ammonium salt in the usual way, is a white, amorphous, insoluble precipitate. It gave the following numbers on analysis :—

0·2121 gram substance gave 0·1045 gram Ag.

	Theory. $C_{12}H_{12}O_4Ag_2$.	Found.
Ag.....	49·54 per cent.	49·27 per cent.

Orthophenylenedipropionic acid appears also to be formed by the action of reducing agents on orthophenylenediacrylic acid.

Tetrabromo-orthophenylenedipropionic Acid,

$C_6H_4(CHBr{\cdot}CHBr{\cdot}COOH)_2$.

This acid is produced by the direct combination of orthophenylenediacrylic acid with 2 mols. of bromine, thus:—

$$C_6H_4(CH:CH{\cdot}COOH)_2 + 2Br_2 = C_6H_4(CHBr{\cdot}CHBr{\cdot}COOH)_2.$$

In preparing it, pure orthophenylenediacrylic acid is allowed to stand under a glass shade containing a small beaker of bromine, for about 24 hours, when it is found to have absorbed exactly 2 molecular proportions of bromine. If care be taken to have the acid in as finely divided a condition as possible, the product obtained is almost pure. After allowing a sample thus prepared to stand for some hours over soda-lime to free it from any excess of bromine, it gave the following numbers on analysis:—

0·2943 gram substance gave 0·2930 gram CO_2 and 0·0598 gram H_2O.

0·2443 gram substance gave 0·3400 gram AgBr.

	Theory. $C_{12}H_{10}Br_4O_4$.	Found.
C.....	26·76 per cent.	27·15 per cent.
H.....	1·86 „	2·25 „
Br.....	59·48 „	59·22 „
O	11·89 „	11·38 „

A direct experiment was made to prove that the acid was really formed quantitatively from orthophenylenediacrylic acid according to the equation given above. 0·731 gram of orthophenylenediacrylic acid, after being subjected to the action of bromine and the excess of the latter removed by exposure to soda-lime, weighed 1·808 gram; 1·077 gram of bromine or 147·3 per cent. had therefore been absorbed, whereas theoretically an absorption of bromine equivalent to 146·3 per cent. should have taken place.

Tetrabromo-orthophenylenedipropionic acid is sparingly soluble in benzene, light petroleum, bisulphide of carbon, and chloroform. When boiled with water or alcohol, it is decomposed with elimination of hydrogen bromide. Heated in a test-tube, bromine and hydrogen bromide are evolved, and a carbonaceous residue is left.

Several experiments were next tried with the object of obtaining orthophenylenedipropiolic acid from this tetrabromide, according to the following equation:—

$$C_6H_4(CHBr{\cdot}CHBr{\cdot}COOH)_2 + 6KOH = C_6H_4{\cdot}(C:C{\cdot}COOK)_2 + 4KBr + 6OH_2.$$

For this purpose, the action of caustic potash under various conditions was tried; and although on several occasions small quantities of an acid free from bromine were obtained, the amount was too small for analysis. Probably by converting the tetrabromo-acid into its ethylic salt, and then hydrolysing with the calculated quantity of alcoholic potash, better results will be obtained; experiments in this direction are in progress.

Formation of Tetrahydronaphthalenedicarboxylic Acid from Ethylic Ortho-xylylenedimalonate.

This interesting synthesis, which has already been referred to in the introduction, was carried out in the following way:—

Ethylic ortho-xylylenedimalonate was dissolved in about 10 vols. of ether and slowly added to an ethereal solution of sodic ethylate containing the latter in the proper proportion to form the disodium-derivative. An ethereal solution of the calculated quantity of iodine was then slowly run in, the whole being well agitated and cooled during the operation. At first the colour of the iodine disappeared at once, but more slowly towards the end of the reaction; after all the iodine had been added, the solution had a decidedly yellow tinge. Water was now added, the ethereal solution separated, washed with water, dried over calcic chloride, and the ether distilled off; an almost colourless oil remained which was at once hydrolysed by boiling with alcoholic potash. After evaporating the alcohol, dissolving in water, acidifying with dilute sulphuric acid, and extracting with ether, a quantity of an almost colourless syrup was obtained which, when heated to 185°, gave off water and carbonic anhydride, and was converted into the anhydride of tetrahydronaphthalenedicarboxylic acid; this was easily identified with that obtained by the action of ortho-xylylene dibromide on the disodium-derivative of ethylic acetylenetetracarboxylate (as described page 12), not only from its melting point, 184°, but also from the fact that when boiled with caustic soda it is converted into tetrahydronaphthalenedicarboxylic acid, melting at 199°, and otherwise identical in every respect with that obtained from ethylic acetylenetetracarboxylate.

I cannot finish this paper without expressing my sincere thanks to Professor Adolf v. Baeyer, in whose laboratory these experiments were carried out, not only for the many suggestions he made, but also for the valuable help he rendered in overcoming the many difficulties of the experimental part.

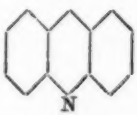
II.—*Synthetical Formation of Closed Carbon-chains in the Aromatic Series.* Part II.

By F. Stanley Kipping, Ph.D., D.Sc.

Among the vast number of aromatic hydrocarbons, there are many which have been proved to contain two or more benzene nuclei condensed together, that is to say, they are compounds in which certain carbon-atoms are common to both rings, as for example, naphthalene, anthracene, and phenanthrene.

Other substances are known in which one or more atoms of nitrogen displace one or more atoms of carbon in the closed chain, without producing any alteration in the fundamental constitution of the compound; for instance, quinoline, acridine, and pseudoanthroline.

Quinoline.

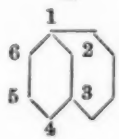


Acridine.

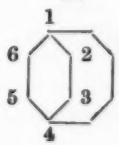
Pseudoanthroline.

Now, in examining the formulæ which, according to the present theoretical views, have been proved, both by synthetical and analytical methods, to represent the constitution of the compounds mentioned, it is at once evident that the carbon-atoms which are common to any two rings are situated in the ortho- or 1 . 2-position; up to the present time no compound has been obtained in which two carbon-atoms, occupying the meta- or para-position in one closed chain, enter into the formation of the adjoining one; although in the present state of our knowledge of the formation of closed chains there is no *à priori* reason why such compounds should not exist, and why, for instance, isomeric naphthalenes having the formulæ—

I.



II.



could not be formed. In formula I, two carbon-atoms in the meta-position would be common to both rings, and in formula II this would be the case with two carbon-atoms in the para-position. It seemed an interesting subject for research to attempt to synthesise

either such hydrocarbons themselves, or some derivatives of them, in order to obtain experimental evidence as to the possibility of the existence of compounds so constituted.

In Part I of this paper (this vol., p. 1), W. H. Perkin, jun., has described the synthesis of naphthalene from ortho-xylene by a series of reactions, which forms an additional proof that condensation of the benzene-rings takes place in the ortho-position; if isomeric naphthalenes, or derivatives of such compounds, can be produced, it seemed probable that they would be obtained in an exactly similar manner when meta- or para-xylene was used in place of the ortho-compound. Acting on the kind suggestion of Perkin, I undertook to work out this research, and proceeded in the following manner: meta-xylene was treated with bromine, and the meta-xylylene bromide thus obtained was acted upon, in ethereal solution, with ethylic chloromalonate and sodic ethylate when ethylic meta-xylylenedichlorodimalonate was formed, the reaction being expressed by the following equation:—

$$C_6H_4\begin{matrix}CH_2Br(1)\\CH_2Br(3)\end{matrix} + 2CHCl(COOC_2H_5)_2 + 2C_2H_5\cdot ONa =$$
$$C_6H_4\begin{matrix}CH_2\cdot CCl(COOC_2H_5)_2(1)\\CH_2\cdot CCl(COOC_2H_5)_2(3)\end{matrix} + 2C_2H_5\cdot OH + 2NaBr.$$

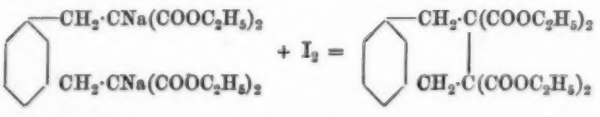
By treating this product with reducing agents, the chlorine is displaced by hydrogen, and ethylic meta-xylylenedimalonate formed, thus:—

$$C_6H_4[CH_2\cdot CCl(COOC_2H_5)_2]_2 + 2H_2 = C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2 + 2HCl.$$

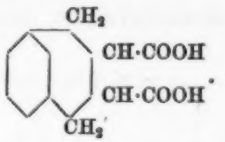
On adding sodic ethylate to an ethereal solution of this ethylic salt, a disodium-derivative is produced, thus:—

$$C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2 + 2C_2H_5\cdot ONa =$$
$$C_6H_4[CH_2\cdot CNa(COOC_2H_5)_2]_2 + 2C_2H_5\cdot OH.$$

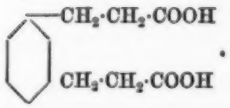
By appropriate treatment with iodine or bromine, it was thought that the sodium would be eliminated, and from this compound a tetrahydrometanaphthalene-derivative obtained according to the following equation:—



from which, by hydrolysis and removal of two carboxyl-groups, tetrahydrometanaphthalenedicarboxylic acid would be obtained—



A dicarboxylic acid was in fact obtained, which was at first thought to be the desired compound; on careful examination, however, it was found that it contained no meta-ring, but was simply metaphenylene-dipropionic acid—



It will be seen that this acid differs in composition from the hypothetical metanaphthalene-derivative only by two atoms of hydrogen, and that, therefore, analysis alone would be insufficient to distinguish between them with certainty; it can be proved beyond doubt, however, that no closed ring has been formed in the above reactions, for when ethylic meta-xylylenedimalonate is directly hydrolysed without previous treatment with sodic ethylate and iodine (or bromine), the dicarboxylic acid which is ultimately obtained is identical with that which was supposed to be a tetrahydrometanaphthalene-derivative.

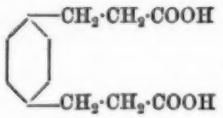
It is difficult to explain what takes place when the above-mentioned sodium-derivative is treated with iodine (or bromine), but it would seem that the halogen destroys a portion of the substance, with formation of hydriodic (or hydrobromic) acid, which then reacts on the remainder, reproducing the ethereal salt and the respective haloïd sodium compound.

In spite of the failure of these experiments to produce a meta-closed ring, the conclusion was not justified that a para-ring could not be formed, since, according to the present theories held regarding the constitution of the numerous compounds containing a pyridine-ring, and of the paraquinones, a union of two atoms in the para-position either directly or through the interposition of other atoms is assumed.

Para-xylene was therefore prepared, and submitted to a series of reactions exactly in the same way as in the case of the meta-hydrocarbon; the sodium compound of ethylic para-xylylenedimalonate was obtained, and treated with iodine (or bromine) in the hope of forming a tetrahydroparanaphthalene-derivative.

But here again no closed ring could be produced; when iodine is used the reaction which takes place appears to be similar to that suggested as the most probable in the case of the meta-compound, and the dicarboxylic acid which is the ultimate product is not a

tetrahydroparanaphthalene-derivative, but simply paraphenylenedipropionic acid—

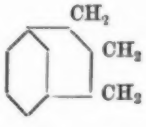


This was proved in a manner similar to that already described. When bromine is used, the reaction is quite different; substitution takes place, and ethylic para-xylylenedibromodimalonate is formed, most probably as expressed by the equation—

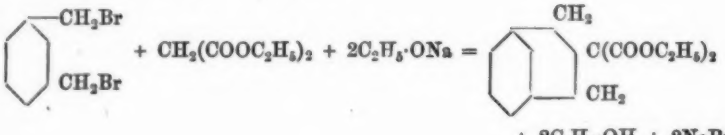
$$2C_6H_4[CH_2\cdot CNa(COOC_2H_5)_2]_2 + 2Br_2 = C_6H_4[CH_2\cdot CBr(COOC_2H_5)_2]_2 + 2NaBr + C_6H_4[CH_2\cdot CNa(COOC_2H_5)_2]_2.$$

From these experiments, then, the conclusion may be drawn that compounds containing rings condensed together in the meta- or para-position are incapable of existence, otherwise they would have been formed by the methods which have been described; now this may be so for one of two reasons—either on account of the relative positions of the two rings, or because of the number of carbon-atoms which would form the reduced ring; in tetrahydrometanaphthalene, as will be seen from the figures already given, there would be seven, in tetrahydroparanaphthalene there would be eight carbon-atoms in the larger closed chain.

To help to a decision on this point, experiments were made with the object of obtaining a derivative of a compound having the formula—



which, like naphthalene itself, would contain six atoms in each ring; a compound of this character should be obtained by treating meta-xylylene bromide with 2 mols. of sodic ethylate and 1 mol. of ethylic malonate, according to the equation—



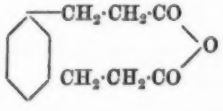
$$+ 2C_2H_5\cdot OH + 2NaBr,$$

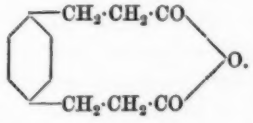
in a manner exactly similar to that in which hydrindonaphthene-

derivatives were prepared by Perkin (see Part I, this vol., p. 7). But, although the experiment was repeated several times under varied conditions, no such compound could be obtained; the reaction was evidently of a very complicated nature, and yielded a resinous mass from which no definite product could be isolated. It seems, therefore, that the non-formation of a meta- or para-ring in any of these cases is due, not entirely to the number of atoms which would go to form the ring, but also, and perhaps wholly, to its relative position.

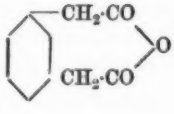
It is a general law in the chemistry of the aromatic compounds that no substance can be obtained in which a ring of any sort is joined to the benzene nucleus in other than the ortho-position, *e.g.*, the coumarins, carbostyrile-derivatives, quinoxaline, &c.; the simplest bibasic acid—phthalic—is readily converted into the anhydride, whilst the isomeric meta- and para-anhydrides have not yet been prepared.

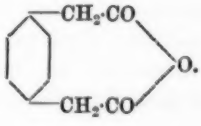
The two isomeric meta- and para-phenylenedipropionic acids obtained in this research by reactions already described, were of considerable theoretical interest, owing to the fact that if anhydrides could be obtained from them they would contain a closed ring in the meta- and para-position respectively, as shown by the formulæ





Attempts were therefore made in this direction, but without success, and it was thought that perhaps this was owing to the large number of atoms which would have to take part in the formation of the closed ring: in the fatty series, as is well known, many dicarboxylic acids can be converted into anhydrides, but whether this is possible or not depends on the relative positions of the carboxyl-groups, that is, on how many carbon-atoms go to form the anhydride-ring. To throw some light on this question, meta- and para-xylylene cyanides were prepared, and from them, by hydrolysis, the corresponding phenylene-diacetic acids; it seemed possible that these compounds, containing as they do one atom of carbon less in each of the side chains, would be more capable of forming anhydrides; these would have the formulæ





No anhydride, however, could be obtained from either of these acids, and the conclusion drawn from all the experiments briefly described above confirms the general law that no exterior ring in the meta- or para-position can be formed.

Meta-xylylene Bromide, $C_6H_4<^{CH_2Br\ (1)}_{CH_2Br\ (3)}$.

Meta-xylylene bromide was first obtained by Colson (*Compt. rend.*, **99**, 40), by brominating boiling meta-xylene; in preparing large quantities of this substance, I have found that the following method gives the best results:—50 grams of pure meta-xylene, placed in a retort connected with a long reflux condenser, are heated in an oil-bath to 125—130°, 160 grams of bromine are then added by means of a dropping funnel inserted into the tubulus of the retort; at first the bromine may be added tolerably quickly, but later on, when the meta-xylene is partially converted and red fumes escape up the condenser, the halogen must be added slowly, otherwise loss is incurred. The hydrogen bromide, which is evolved in large quantities during the reaction, is absorbed by conducting it into a concentrated solution of caustic soda.

When all the bromine has been added, the contents of the retort, which ought to be only slightly coloured, are poured out and left 24 hours in a cool place to crystallise; the mother-liquor is drained off, and the crystals, after lying for some time on a porous plate, are purified by recrystallisation from light petroleum; meta-xylylene bromide is thus obtained in the pure state as a colourless solid melting at 77°, the melting point given by Colson (*loc. cit.*). From 50 grams of meta-xylene the quantity of pure bromide obtained is not very large, the mother-liquor can, however, be worked up for a less pure product. In consequence of the painful effect of the vapour on the eyes, it is best when using meta-xylylene to work as much as possible in the open air.

Ethylic Meta-xylylenedichlorodimalonate,
$C_6H_4[CH_2{\cdot}CCl(COOC_2H_5)_2]_2$.

This compound is obtained by the action of ethylic chloromalonate and sodic ethylate on meta-xylylene bromide; 4·4 grams of sodium, dissolved in as small a quantity of alcohol as possible, are mixed with about 10 volumes of pure ether, and a solution of 37·8 grams of ethylic chloromalonate in 500 c.c. pure ether slowly added; after well cooling the mixture, 25·5 grams of finely-powdered meta-xylylene bromide are thrown in, and the whole well shaken. The white precipitate which is at first formed is the sodium-derivative of ethylic

chloromalonate, but as the meta-xylylene bromide dissolves, a lively reaction commences and the ether begins to boil, the sodium-derivative being decomposed with formation of ethylic meta-xylylene dichlorodimalonate and sodium bromide. The mixture is then heated on a water-bath for a couple of hours, great care being taken to shake occasionally, otherwise there is considerable danger of the ether boiling over from the bumping which always occurs; water is subsequently added, the ethereal solution washed and separated, dried over calcium chloride, and the ether distilled off.

Ethylic meta-xylylene dichlorodimalonate remains as a thick, yellowish oil, which even after long standing over sulphuric acid in a vacuum shows no signs of crystallising; on analysis the following results were obtained:—

I. 0·1615 gram substance gave 0·1015 gram AgCl.
II. 0·2805 „ „ 0·1660 „ „

	Calculated for $C_{22}H_{28}O_8Cl_2$.	Found. I.	Found. II.
Cl	14·4 p. c.	15·5	14·6 p. c.

The second analysis was made from a different sample, the ethereal salt used in (I) having been found to contain a trace of unchanged meta-xylylene bromide.

When the calculated quantities of ethylic chloromalonate and meta-xylylene bromide are carefully weighed, the resulting ethylic meta-xylylene dichlorodimalonate is almost pure and the yield quantitative.

Ethylic Meta-xylylenedimalonate, $C_6H_4[CH_2{\cdot}CH(COOC_2H_5)_2]_2$.

When the chlorine-compound described above is dissolved in about 15 volumes of glacial acetic acid and a small quantity of zinc-dust added, reduction at once commences, the mixture becoming quite warm.

The process is best carried out by adding the zinc-dust in very small quantities at a time for about an hour, the whole being constantly shaken in a long-necked flask; at the end of this time, the solution becomes very thick, owing to the formation of zinc acetate, and reduction proceeds only very slowly; water is therefore added, the mixture warmed on the water-bath, and the ethereal salt extracted with ether, not only from the solution but also from the undissolved zinc-dust, which retains a considerable quantity of the substance; the ethereal solution after washing, first with water, and then with sodium carbonate solution to get rid of acetic acid, is dried over anhydrous

potassium carbonate and the ether distilled off. The oil which remains still contains a considerable proportion of the unchanged chlorinated derivative, the reduction is therefore repeated in exactly the same manner; it was found, however, that even after three such treatments a trace of chlorine is still present; the best results are obtained when only small quantities at a time are operated upon.

In order to prepare this substance pure for analysis, use is made of the sodium-derivative; when the calculated quantity of sodium, dissolved in absolute alcohol and mixed with about 10 volumes of ether, is added to a weak ethereal solution of ethylic meta-xylylene dimalonate, a white precipitate of the disodium-derivative is formed. This is washed with ether on the filter-pump as quickly as possible, and then thrown into water or dilute sulphuric acid, when it is at once decomposed, yielding ethereal salt and sodium hydrate (or sulphate). The oil which separates is extracted with ether, and after drying the ethereal solution with calcium chloride, it is treated again, exactly as before, with the calculated quantity of sodic ethylate; the precipitate is washed as above, decomposed with dilute sulphuric acid, the solution extracted with ether, and the product isolated in the usual manner.

Ethylic meta-xylylenedimalonate is thus obtained in the pure state as a thick, colourless oil, which, however, could not be obtained in the crystalline form; it is readily soluble in ether, alcohol, acetic acid, &c., but insoluble in water.

The following results were obtained on analysis :—

0·1550 gram substance gave 0·3522 gram CO_2 and 0·1016 gram H_2O.

	Calculated for $C_{22}H_{30}O_8$.	Found.
C.....	62·56 per cent.	61·97 per cent.
H.....	7·11 „	7·28 „
O.....	30·33 „	30·75 „

The sodium-derivative of this ethereal salt is a white solid, which, however, on account of its extremely hygroscopic nature, soon decomposes on exposure to the air. To prepare a sample for analysis, a few grams of ethylic meta-xylylenedimalonate are dissolved in a large volume of dry ether, and the calculated quantity of sodic ethylate, mixed with about 10 volumes of ether, added to the solution. The flask is tightly corked, and the mixture after being well shaken is allowed to stand, in order that the precipitate may settle; when it has completely subsided, it is washed twice by decantation with pure ether (the air being excluded as much as possible), and after draining

off the ether as far as possible, quickly transferred to a tared stoppered weighing-bottle.

After standing in a vacuum over sulphuric acid, a sodium determination was made, from which the following result was obtained :—

0·4055 gram substance gave 0·1215 gram sodic sulphate.

	Calculated for $C_{22}H_{28}Na_2O_8$.	Found.
Na	9·9 per cent.	9·7 per cent.

Experiments were now made to obtain a tetrahydrometanaphthalene-derivative from the disodium malonate.

The following is a description of the methods employed :—The calculated quantity of sodium, dissolved in alcohol and mixed with about 10 volumes of ether, is added to a weak ethereal solution of ethylic meta-xylylenedimalonate, and after allowing the sodium-derivative to separate out, which takes but a very few moments, a very slight excess of the calculated quantity of iodine, also dissolved in ether, is added and the mixture vigorously shaken. The dark-brown colour of the iodine rapidly disappears, and in a few minutes the reaction is completed, the slightly brown colour of the solution being due to the small excess of the halogen used; after adding water to dissolve the sodic iodide, and removing the trace of iodine by means of dilute sulphurous acid, the colourless ethereal solution is washed with water, dried, and the ether distilled off, when the ethereal salt of a tetracarboxylic acid remains behind as a thick, brown oil. This salt is hydrolysed by boiling it for two hours on the water-bath with a solution of potash in methyl alcohol; the alcohol is then evaporated and the potassium-compound dissolved in water; on acidifying this solution with dilute sulphuric acid, a small quantity of impurity is precipitated, this is filtered off and the filtrate extracted repeatedly with ether. The acid obtained on distilling off the ether is a thick, brown oil, which, as it could not be obtained crystalline was, without purifying, converted into the dicarboxylic acid; this is effected by heating it in a flask in a metal-bath at 180—200°, a considerable amount of decomposition taking place, with a copious evolution of carbonic anhydride. When no more gas is given off, the process is at an end, and, on cooling, the contents of the flask become solid. To purify the product, it is now converted into the ethylic salt; for this purpose it is dissolved in dilute ammonia, the excess of the latter removed by standing in a vacuum over sulphuric acid, and the solution filtered to get rid of a small quantity of oil which is present; silver nitrate is then added to the filtrate, and the silver salt thus formed is washed with water on the filter-pump. After careful drying, it is suspended

in ether, treated with an excess of ethyl iodide, and boiled on the water-bath with reflux condenser for about two hours, whereby the silver salt is completely decomposed. The silver iodide is filtered off and well washed with warm ether, the washings added to the filtrate, and the ethereal salt obtained by distilling off the ether; it is, however, still impure, and is therefore submitted to fractional distillation under diminished pressure. A trace of ethyl iodide first comes over, the thermometer then rapidly rises, and the whole distils between 200° and 250° (60 mm. pressure); the high boiling portion is again fractioned, when almost the whole distils over without decomposition constantly at 247—250° as a colourless, mobile oil. An analysis was now made, which, however, agreed equally well for either of the two formulæ—

$$C_6H_4\begin{<}\begin{matrix}CH_2CH(COOC_2H_5)\\ |\\ CH_2CH(COOC_2H_5)\end{matrix} \quad \text{or} \quad C_6H_4\begin{<}\begin{matrix}CH_2{\cdot}CH_2(COOC_2H_5)\\ \\ CH_2{\cdot}CH_2(COOC_2H_5)\end{matrix}.$$

As the acid itself would probably crystallise, and could therefore be more easily obtained in a high degree of purity, further attempts to purify the ethereal salt were considered unnecessary, and it was converted into the acid by boiling with a solution of pure potash in methyl alcohol; when hydrolysis was complete, the solution was evaporated to dryness, the potassium salt dissolved in water, dilute sulphuric acid added in excess, and the organic acid extracted with ether. After isolating the product in the usual way, and recrystallising it from boiling water, it was obtained in beautiful glistening plates; an analysis was made which again did not decide whether the ring formation had taken place or not, and other means had therefore to be employed to settle this point beyond doubt. Metaphenylenedipropionic acid was prepared according to the methods described later on, and as this substance, which must have the formula

$$C_6H_4(CH_2{\cdot}CH_2{\cdot}COOH)_2,$$

is identical with the acid obtained above, it is quite clear that no meta-ring had been formed by the action of iodine on the sodium-derivative of ethylic meta-xylylenedimalonate.

Another attempt to obtain a tetrahydrometanaphthalene-derivative was therefore made; in this case, bromine was used instead of iodine, and since there was a considerable loss from decomposition on heating the tetracarboxylic acid in the metal-bath, another method for eliminating the two carboxyl-groups was adopted. The following is an account of the manner in which the experiment was carried out: to a solution of 1·4 grams of sodium dissolved in 15 grams of absolute alcohol, and mixed with 50 c.c. of pure ether, 12 grams of ethylic meta-xylylene-

dimalonate in ethereal solution were added, and the mixture allowed to stand in a freezing mixture until the sodium compound had completely subsided; 4·6 grams of bromine were then gradually dropped in, the whole being kept well cooled. Each drop of bromine was immediately absorbed, the few last only causing the solution to assume a slightly yellow colour.

The product of this reaction was separated as already described in the experiment with iodine, and the ethereal salt hydrolysed by boiling it for two hours with alcoholic potash; 9 grams of the tetracarboxylic acid were thus obtained in the form of a brown oil which could not be got to crystallise; it was therefore mixed with about three times its weight of water, and heated in a sealed tube, first at 110°, then, after opening the capillary to get rid of the carbonic anhydride, at 150°, and finally again at 180° until the evolution of gas entirely ceased.

The contents of the tube, when cool, consisted of two layers; the undermost after standing for some time solidified almost completely, whilst the upper one was filled with colourless crystals. After purification, these crystals were found to be identical with the acid obtained before—viz., metaphenylenedipropionic acid. The solid mass which formed the lower layer was dissolved in boiling water, and, after filtering, allowed to crystallise; again the same acid was proved to have been formed, and the quantity obtained was from 1½—2 grams. About 3 grams of a black resinous mass from which no crystalline product could be isolated remained on the filter; the mother-liquor from the acid yielded nothing but a further quantity of impure metaphenylenedipropionic acid, which took the form of a slightly yellow oil.

The result of these two experiments showed, therefore, that by acting on the sodium compound of ethyl meta-xylylenedimalonate with bromine or iodine no meta-ring is produced, and the same compound is ultimately obtained after hydrolysis and elimination of two carboxyl-groups, whether this reaction is carried out or not; the possibility that such a ring can exist is thereby rendered improbable.

Meta-xylylenedimalonic Acid, $C_6H_4[CH_2{\cdot}CH(COOH)_2]_2$.

When the crude ethylic salt of this acid (see p. 27) is boiled with excess of potash in methylic alcohol until no oil is precipitated on addition of water, hydrolysis is complete; this is the case after about two hours.

The alcohol is distilled off, and the potassium salt which is obtained on evaporation to dryness is dissolved in water; the addition of sulphuric acid in excess produces a slight turbidity, the solution is

therefore filtered, and the product extracted from the filtrate by shaking out about 10 times with pure ether. When the ether is distilled off, meta-xylylenedimalonic acid remains behind as a thick, slightly brown oil, which is readily soluble in water, alcohol, and ether. Unfortunately it could not be obtained in the crystalline form, so no analysis of it was made; that its constitution is that represented by the above formula is, however, proved by its method of formation and by its decompositions, also by a comparison with the isomeric para-acid described later on, to which it is strictly analogous.

Metaphenylenedipropionic Acid, $C_6H_4(CH_2{\cdot}CH_2{\cdot}COOH)_2$.

On heating the tetracarboxylic acid just described, it is readily converted into metaphenylenedipropionic acid with elimination of 2 mols. of carbonic anhydride.

This conversion may be effected in two different ways:—First, meta-xylylenedimalonic acid is heated in a small flask in a metal-bath; as soon as the temperature rises above 100° carbonic anhydride begins to be evolved, the evolution becoming more rapid as the temperature rises; after keeping the bath at about 180° for some time, no more carbonic anhydride is given off, and the change is complete. On cooling, the dark-brown oil solidifies to an almost solid cake, which is dissolved in hot water, boiled with animal charcoal, and the solution filtered; the new acid crystallises from the filtrate in beautiful colourless plates, and is obtained pure by three recrystallisations from boiling water.

The second method for the preparation of this substance takes up far more time, but it is preferable as the yield is far better: meta-xylylenedimalonic acid is dissolved in about three times its volume of water, and heated in a sealed tube for one hour at 100—120°; the tube is then allowed to cool, and the capillary opened to permit of the escape of the carbonic anhydride; after re-sealing, it is heated again at 150° for an hour, the gas formed allowed to escape, and the contents of the tube raised to a temperature of about 180° for some considerable time. The tetrabasic acid is now completely decomposed, and the liquid which was at first homogeneous is found, after cooling, to have separated into two layers; the bottom one solidifies completely whilst the top one is filled with leaf-like crystals. To purify the product, the whole is collected, and the residue, after spreading on a porous plate to remove traces of oil, is dissolved in boiling water, and the solution filtered. On cooling, pure metaphenylenedipropionic acid separates in magnificent, lustrous, colourless plates. It was dried

over sulphuric acid, then at 100°, and analysed with the following result:—

0·1690 gram substance gave 0·4010 gram CO_2 and 0·0985 gram H_2O.

	Calculated for $C_{12}H_{14}O_4$.	Found.
C	64·86 per cent.	64·71 per cent.
H	6·31 „	6·47 „
O	28·83 „	28·82 „

Metaphenylenedipropionic acid when pure melts at 146—147°; it is moderately soluble in hot, but almost insoluble in cold water, and dissolves easily in ether and alcohol. On precipitating a neutral solution of the ammonium salt with silver nitrate, the silver salt falls down as a white amorphous precipitate; after washing well and drying over sulphuric acid in a vacuum, it was analysed with the following result:—

0·3318 gram substance gave 0·1638 gram Ag.

	Calculated for $C_{12}H_{12}Ag_2O_4$.	Found.
Ag.....	49·54 per cent.	49·37 per cent.

This salt is very stable, and does not darken when exposed to diffused light.

In an aqueous neutral solution of the ammonium salt, lead acetate gives a white, amorphous precipitate, copper sulphate a light, bluish-green precipitate, and zinc sulphate a white, crystalline precipitate. Barium chloride gives no reaction.

An experiment was made to try and obtain the anhydride of this acid by heating a small quantity for half an hour in a metal-bath at a temperature of 250°. The acid darkened in colour, traces of water were evolved, and a slight amount of decomposition took place; on heating more strongly over the naked flame, a brown oil distilled and almost immediately solidified. After washing the product with ether on a porous plate, an almost colourless substance was obtained which showed the same melting point as the original acid; no anhydride was therefore formed.

Methylic Metaphenylenedipropionate.

This ethereal salt is obtained in the usual manner by treating argentic metaphenylenedipropionate with methyl iodide.

The pure dry silver salt is mixed with an excess of methyl iodide dissolved in 10 volumes of ether, and the mixture heated on the

water-bath with reflux condenser for about five hours; at the end of this time, the silver salt will be entirely decomposed. To isolate the product, the silver iodide is filtered off, washed with ether, and the washings added to the filtrate; on distilling off the ether, a thick colourless oil remains behind, which in a short time solidifies to a hard cake of crystals; it is purified by spreading on a porous plate and recrystallising from dilute methyl alcohol. Methylic metaphenylenedipropionate is thus obtained pure in the form of colourless plates, and on analysis the following results were obtained:—

0·1570 gram substance gave 0·3865 gram CO_2 and 0·1065 gram H_2O.

	Calculated for $C_{14}H_{18}O_4$.	Found.
C	67·2 per cent.	67·14 per cent.
H	7·2 „	7·53 „
O	25·6 „	25·33 „

This substance is very easily soluble in ether, alcohol, and benzene, but only sparingly in cold methyl alcohol; it melts at 51°, and when heated in small quantities at a time distils at a high temperature almost without decomposition.

Ethylic Metaphenylenedipropionate.

This is obtained in a manner exactly similar to that used in the preparation of the methyl salt just described; it is a colourless oil, which boils at 247—250° (60 mm. pressure) without decomposition. The analysis gave the following results:—

0·1243 gram substance gave 0·3171 gram CO_2 and 0·0866 gram H_2O.

	Calculated for $C_{16}H_{22}O_4$.	Found.
C	69·07 per cent.	69·55 per cent.
H	7·91 „	7·74 „
O	23·02 „	22·71 „

Para-xylylene Bromide, $C_6H_4(CH_2Br)_2$.

This is prepared by brominating para-xylylene in the same way as described under the meta-compound. When the reaction is finished, the product is allowed to stand for a short time; it then solidifies, and is purified by simply spreading on a porous plate. The yield obtained ranges from 85—90° of the theoretical. The action of the vapour of this substance on the eyes is extremely painful, it is advisable, therefore, to work as much as possible in the open air.

Ethylic Para-xylylenedichlorodimalonate, $C_6H_4[CH_2{\cdot}CCl(COOC_2H_5)_2]_2$.

36·8 grams of ethylic chloromalonate are dissolved in about 500 c.c. of ether, the calculated quantity of sodium dissolved in absolute alcohol and mixed with 10 volumes of ether added, and then 25 grams para-xylylene bromide thrown in and the mixture vigorously shaken. The sodium-derivative of ethyl chloromalonate first forms, but on continued shaking the para-xylylene bromide dissolves and the reaction commences; no appreciable warming of the mixture, however, is noticed.

After heating on the water-bath with reflux condenser for about four hours, care being taken on account of the great tendency of the mixture to bump, water is added to dissolve the sodium bromide, and the ethereal solution is then separated and dried. When the ether is distilled off, ethyl para-xylylenedichlorodimalonate remains as a thick, brownish oil, the amount obtained being in accordance with theory. On standing for some hours, this oil is converted into a crystalline solid mass; the adhering mother-liquor is removed by spreading on a porous plate, and the product purified by recrystallisation from alcohol. In this way the ethereal salt is obtained in large, colourless, six-sided plates; it melts at 86—87°, is readily soluble in alcohol, ether, light petroleum, acetic acid, &c., but is insoluble in water. A chlorine determination gave the following result:—

0·3715 gram substance gave 0·2200 gram AgCl.

	Calculated for $C_{22}H_{28}Cl_2O_8$.	Found.
Cl.....	14·4 per cent.	14·6 per cent.

Ethylic Para-xylylenedimalonate, $C_6H_4[CH_2{\cdot}CH(COOC_2H_5)_2]_2$.

To prepare this substance, the chlorine-compound just described is reduced with zinc-dust and acetic acid in exactly the same way as the corresponding meta-ethereal salt. About 15 grams are dissolved in 15 c.c. of glacial acetic acid, and a small quantity of zinc-dust added; as the reduction commences, the mixture becomes warm. After constant shaking for about an hour with frequent addition of small quantities of zinc-dust, water is added and the mixture warmed on the water-bath in order to dissolve the zinc acetate; the whole is then shaken out with ether several times, the ethereal solution washed with water and sodium carbonate to get rid of the acetic acid, dried over anhydrous potassium carbonate, and the ether distilled off. Ethyl para-xylylenedimalonate remains behind: as in the case of the

meta-derivative, however, a very considerable quantity of the chlorine compound still remains unreduced; it is necessary, therefore, to repeat the treatment with zinc-dust and acetic acid, and it was found best to work with only small quantities of the substance, and submit it to at least three reductions. It is thus obtained as a slightly yellow oil, which if allowed to remain over sulphuric acid in a vacuum, in a few days deposits a quantity of colourless crystals; these are freed from oil by spreading them on a porous plate and washing with a trace of alcohol, when the substance is obtained quite pure; after drying in a vacuum, an analysis was made with the following results:—

0·2285 gram substance gave 0·5215 gram CO_2 and 0·1495 gram H_2O.

	Calculated for $C_{22}H_{30}O_8$.	Found.
C	62·56 per cent.	62·24 per cent.
H	7·11 „	7·27 „
O	30·33 „	30·49 „

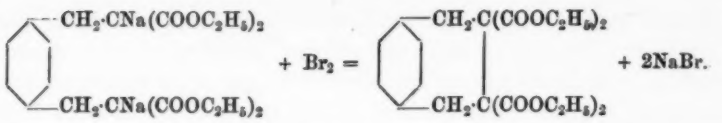
Ethylic para-xylylenedimalonate is a fine, white, crystalline substance, which melts at 51°; it is very readily soluble in ether, far less so in alcohol, and insoluble in water. This ethereal salt, like the corresponding meta-derivative, forms a compound with sodium, which is obtained as a white precipitate when the calculated quantity of sodic ethylate and ethyl para-xylylenedimalonate are mixed together in ethereal solution. The precipitate is washed with pure dry ether, by decantation, the same precautions being taken to exclude the air as were described in the preparation of the meta-compound, thrown on to a filter and transferred as quickly as possible to a tared stoppered weighing bottle; after standing in vacuum over sulphuric acid, a sodium estimation was made, of which the following was the result:—

0·5010 gram substance gave 0·1520 gram Na_2SO_4.

	Calculated for $C_{22}H_{28}Na_2O_8$.	Found.
Na	9·9 per cent.	9·8 per cent.

This sodium-derivative is white and extremely hygroscopic, in consequence of which it decomposes quickly on exposure to the air, and immediately on the addition of water or acids, the ethereal salt being regenerated.

It was thought that if this compound were treated with iodine or bromine a tetrahydropara-naphthalene-derivative would be formed, as shown by the following equation:—



The experiment was carried out thus: 12 grams of ethyl para-xylylenedimalonate, dissolved in about 50 c.c. of ether, were mixed with an ethereal solution of sodic ethylate, containing 1·4 grams of sodium, and then 5 grams of bromine slowly added. The colour of the bromine disappeared instantly on coming into contact with the sodium-compound, the last few drops, however, causing a yellow coloration. Water was then added to dissolve the sodium bromide, and after separating and drying the ethereal solution, the ether was distilled off; 16 grams of a heavy oil remained, which on examination was found to contain bromine. On standing for 24 hours in a cool place, crystals were deposited; these were partially separated from the mother-liquor by spreading on a porous plate, and while still on the plate purified by washing with a trace of methyl alcohol, in which the oil is readily soluble, whilst the crystals are hardly dissolved at all. After crystallising from hot methyl alcohol, 4·5 grams of a fine, colourless substance were obtained, and on analysis numbers were found agreeing with the formula—

$$C_6H_4[CH_2CBr(COOC_2H_5)_2]_2.$$

I. 0·2370 gram substance gave 0·3990 gram CO_2 and 0·1090 gram H_2O.

II. 0·2900 gram substance gave 0·1820 gram bromide of silver.

	Calculated.	Found. I.	Found. II.
C	45·6 p. c.	45·9	—
H	4·8 „	5·1	—
Br	27·5 „	—	26·5 per cent.

This substance is, therefore, ethylic para-xylylenedibromodimalonate; it is only sparingly soluble in cold, but readily in hot methyl alcohol, from which it crystallises on cooling in magnificent, glittering plates, which melt at 107—108°. In order to prove that it really had the constitution assigned to it above, it was treated with zinc-dust and acetic acid, when it was reduced to ethyl para-xylylenedimalonate, and far more readily than the corresponding chlorine-compound. On extracting with ether, a quantity of a crystalline product was obtained, which melted at 51°, and possessed all the properties of ethylic para-xylylenedimalonate, there can therefore be no doubt that this substance is para-xylylenedibromodimalonate.

Since bromine acted on the sodium-compound of ethylic para-xylylenedimalonate in this manner, an experiment was made in exactly the same way, using the calculated quantity of iodine, however, instead of bromine; the product of the reaction was a thick brown oil, which owing to the impurities present could not be got to crystallise; on heating a few drops in a test-tube, violet vapours were evolved, and traces of iodine sublimed. The analysis of the impure substance showed that it contained only from 2 to 2½ per cent. of iodine, which was present in the combined state, so that ethylic para-xylylenediiododimalonate was either not formed at all or only in very small quantities, as this compound would contain 38 per cent. of iodine. The oil was, therefore, hydrolysed and converted into the dicarboxylic acid by heating it in a sealed tube at 180° until there was no further evolution of carbonic anhydride; the product was isolated, recrystallised, and when pure its melting point was found to be 223—224° (the melting point of para-phenylenedipropionic acid). In this case, also, it is clear that no ring formation had taken place.

Para-xylylenedimalonic Acid, $C_6H_4[CH_2{\cdot}CH(COOH)_2]_2$.

When the ethereal salt of this acid, which has been already described, is boiled for about four hours on a water-bath, with excess of potash in methyl alcohol, hydrolysis is complete. The solution is then evaporated to dryness to drive off the alcohol, the residual potassium salt is dissolved in water, and the solution after acidifying with sulphuric acid is extracted repeatedly with ether. When the ethereal solution has been dried over calcium chloride, and the ether distilled off, para-xylylenedimalonic acid is obtained as a thick syrup, which on standing solidifies to a hard cake. This is spread on a porous plate in order to get rid of traces of oil, and is then warmed with water and a small quantity of animal charcoal; the filtered solution when allowed to evaporate over sulphuric acid in a vacuum, slowly deposits a finely divided crystalline powder; this is collected and dried, first on a porous plate, and then in a vacuum over sulphuric acid. The analysis gave the following results:—

0·1982 gram substance gave 0·3905 gram CO_2 and 0·0885 gram H_2O.

	Calculated for $C_{14}H_{14}O_8$.	Found.
C	54·2 per cent.	53·7 per cent.
H	4·5 „	4·9 „
O	41·3 „	41·4 „

On heating, para-xylylenedimalonic acid melts at about 195° with

slight decomposition and evolution of carbonic anhydride; the whole mass then suddenly becomes solid, and on continuing to heat melts again at 223° (the melting point of para-phenylenedipropionic acid, see below).

The silver salt was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate; it is a white amorphous substance, and on analysis gave the following result:—

0·5843 gram substance gave 0·3393 gram silver.

	Calculated for $C_{14}H_{10}Ag_4O_8$.	Found.
Ag	58·47 per cent.	58·07 per cent.

The neutral solution of the ammonium salt gives with lead acetate, barium chloride, and calcium chloride, white precipitates of the respective salts.

Paraphenylenedipropionic Acid, $C_6H_4(CH_2{\cdot}CH_2{\cdot}COOH)_2$.

Para-xylylenedimalonic acid when heated is easily decomposed yielding paraphenylenedipropionic acid and 2 mols. of carbonic anhydride. This decomposition is best effected by heating a solution of the acid in about 3 parts of water at 180° in a sealed tube until the evolution of gas ceases, exactly as is described in more detail under the corresponding meta-compound. The reaction in this case goes beautifully, and after cooling, the tube is found to be filled with hard white nodular masses of almost pure paraphenylenedipropionic acid. To purify the product, it is collected and spread on a porous plate to remove traces of oil, and is then dissolved in boiling methyl alcohol; this solution on standing for 24 hours deposits the pure acid in curious nodular aggregates, which after washing with a little alcohol and drying at 100°, were analysed and the following results obtained:—

0·1770 gram substance gave 0·4200 gram CO_2 and 0·1010 gram H_2O.

	Calculated for $C_{12}H_{14}O_4$.	Found.
C	64·86 per cent.	64·73 per cent.
H	6·31 „	6·34 „
O	28·83 „	28·93 „

Paraphenylenedipropionic acid melts at 223—224°; it is only sparingly soluble in cold methyl or ethyl alcohol, and almost insoluble in water.

The silver salt is a white, apparently amorphous precipitate which does not blacken on exposure to diffused light; it was obtained in the

usual way by precipitating the neutral solution of the ammonium salt, and, after drying at 100°, analysed.

0·4300 gram substance gave on ignition 0·2125 gram silver.

	Calculated for $C_{12}H_{12}Ag_2O_4$.	Found.
Ag	49·54 per cent.	49·42 per cent.

The following reactions are shown by a neutral solution of the ammonium salt:—Copper sulphate gives a faint greenish-white amorphous precipitate, sparingly soluble in cold, more readily in hot water; lead acetate throws down the lead salt as a white compound insoluble in water; zinc sulphate and mercuric chloride also give white precipitates, whilst barium chloride and calcium chloride give no precipitate.

The following experiment was then made in the hope of obtaining an anhydride of this acid:—0·3 gram of the pure substance was heated in a test-tube in a metal-bath for half an hour at 300—320°, the acid darkened slightly but no appreciable quantity of water was given off; on raising the temperature considerably and as quickly as possible, the whole distilled over in the form of a thick oil, which, however, at once solidified on the colder parts of the tube, while a very small quantity of carbonaceous matter remained behind. The solid distillate was scraped out of the tube and washed on a porous plate with a small quantity of ether, when an almost colourless substance was obtained which melted at 221—224°; it is therefore clear that no anhydride was formed, but that, on heating, paraphenylenedipropionic acid (m. p. 223—224°) distils unchanged.

Methylic Paraphenylenedipropionate.

By boiling the silver salt of the acid, suspended in ether, with excess of methyl iodide, for about four hours on a water-bath, methylic paraphenylenedipropionate is formed. The solution is filtered, the residual iodide of silver washed well with warm ether, the washings added to the filtrate, and the whole distilled, when the ethereal salt remains behind as a white, crystalline mass. It was purified by spreading on a porous plate and then recrystallising from hot methyl alcohol. The analysis gave the following results:—

0·16225 gram substance gave 0·3995 gram CO_2 and 0·1050 gram H_2O.

	Calculated for $C_{14}H_{18}O_4$.	Found.
C	67·20 per cent.	67·14 per cent.
H	7·20 „	7·19 „
O	25·60 „	25·67 „

Methylic paraphenylenedipropionate is only sparingly soluble in cold methyl alcohol, and separates out from the hot solution, on cooling, in beautiful glittering plates which melt at 115°.

Paraphenylenediacrylic Acid, $C_6H_4(CH : CH\cdot COOH)_2$.

Ethylic ortho-xylylenedichlorodimalonate is readily decomposed on heating it with alcoholic potash into hydrochloric acid, carbonic anhydride, and orthophenylenediacrylic acid.

It was thought interesting to try a similar reaction with an analogous para-derivative. 2 grams of ethylic para-xylylenedibromodimalonate were mixed with a solution of 3 grams of caustic potash in a little alcohol, and the mixture boiled on a water-bath for four hours. After addition of water, the solution was evaporated to dryness, in order to expel the alcohol, and the residual potassium salts dissolved in water; on acidifying with dilute sulphuric acid, a yellowish flocculent substance, probably consisting of impure paraphenylenediacrylic acid, was precipitated; this was not filtered off but the whole extracted with ether, the ethereal solution dried and the ether distilled off. The semi-solid mass which remained was mixed with about 10 c.c. of water and heated in a sealed tube for eight hours at 180°, in order to decompose any tetrabasic acid which might be present. The slightly yellow flocculent substance thus obtained was purified by dissolving it in ammonia, boiling with animal charcoal, and reprecipitating; lastly the substance was well washed with water, dried at 100° and analysed, when the following results were obtained:—

0·2010 gram substance gave 0·4840 gram CO_2 and 0·0892 gram H_2O.

	Calculated for $C_{12}H_{10}O_4$.	Found.
C	66·05 per cent.	65·67 per cent.
H	4·59 ,,	4·96 ,,
O	29·36 ,,	29·37 ,,

Paraphenylenediacrylic acid has been already obtained by Loew (*Annalen*, **231**, 361—384) by the action of sodic acetate and acetic anhydride on terephthalic aldehyde; the product obtained from ethylic para-xylylenedibromodimalonate is identical with Loew's compound, its properties agreeing with those already given by him.

Meta-xylylene Cyanide, $C_6H_4(CH_2\cdot CN)_2$.

The method used in the preparation of this substance is as follows:—13 grams of meta-xylylene bromide are dissolved in alcohol

and a slight excess of the calculated quantity of potassium cyanide, in aqueous solution, added. No reaction takes place at first, but, on warming, potassium bromide begins to crystallise out on the sides of the flask, the reaction being as follows:—$C_6H_4(CH_2Br)_2 + 2KCN = C_6H_4(CH_2{\cdot}CN)_2 + 2KBr$.

By boiling on a water-bath with reflux condenser for a considerable time, the change is completed, the alcohol is then distilled off, and the residue treated with water, whereby the crude meta-xylylene cyanide is precipitated as a brown oil; after separating it from the aqueous solution by means of a separating funnel, it is dried over calcium chloride and fractioned in a vacuum.

Thus purified, it is obtained as a colourless oil, which on cooling almost immediately solidifies to a white crystalline mass; the analyses gave the following results:—

I. 0·2410 gram substance gave 0·6775 gram CO_2 and 0·1120 gram H_2O.

II. 0·2195 gram substance gave 0·6155 gram CO_2 and 0·1095 gram H_2O.

III. 0·22425 gram substance gave 34·75 c.c. Nitrogen. Bar. 718 mm. T. 17°.

	Calculated for $C_{10}H_8N_2$.	Found. I.	II.	III.
C	76·92 p. c.	76·48	76·67	—
H	5·13 „	5·54	5·16	—
N	17·95 „	—	—	17·75 p. c.

Meta-xylylene cyanide is a colourless, crystalline substance melting at 28—29°; it boils under 300 mm. pressure at 305—310°, a certain amount of decomposition taking place. Ether, alcohol, and chloroform dissolve it readily; it is insoluble, however, in water and light petroleum.

Metaphenylenediacetic acid, $C_6H_4(CH_2{\cdot}COOH)_2$.

To obtain this acid, the crude oil formed by the action of potassium cyanide on meta-xylylene bromide is, without further purification, hydrolysed by boiling it on a water-bath with an excess of alcoholic potash solution, whereby it is converted into the potassium salt of metaphenylenediacetic acid.

Hydrolysis does not take place at all readily, and it is necessary to boil for about six hours before the cessation of the evolution of ammonia shows that the reaction is at an end. When this is the case, the alcohol is distilled off and the residue dissolved in water; on acidifying with dilute sulphuric acid, a small quantity of a brown

resinous substance is precipitated and is filtered off; the clear solution is then extracted about 20 times with ether, and after drying the ethereal solution over calcium chloride and distilling off the ether, the acid is left in slightly yellowish crystalline crusts. The product is spread on a porous plate, and while still on the plate, the traces of oil are washed away with a few drops of ether; after two crystallisations from water, it is obtained pure in the form of colourless needles.

It was dried at 100°, and analysed with the following results:—

0·1697 gram substance gave 0·3830 gram CO_2 and 0·0800 gram H_2O.

	Calculated for $C_{10}H_{10}O_4$.	Found.
C	61·86 per cent.	61·54 per cent.
H.....	5·15 „	5·24 „
O.....	32·99 „	33·22 „

Metaphenylenediacetic acid melts at 170°; it is easily soluble in water, alcohol, and ether, but almost insoluble in light petroleum or chloroform: it crystallises from water in beautiful clusters of concentric needles. The yield obtained by hydrolysing the cyanide with alcoholic potash is almost theoretical.

On adding silver nitrate to a neutral aqueous solution of the ammonium salt, the silver salt is obtained as a white amorphous precipitate; after washing well with water, and drying first on a porous plate, and then at 100°, analysis gave the following result:—

0·1305 gram substance gave 0·0685 gram Ag.

	Calculated for $C_{10}H_8Ag_2O_4$.	Found.
Ag.....	52·8 per cent.	52·5 per cent.

In an aqueous solution of the ammonium salt, lead acetate gives a white amorphous precipitate, but with sulphate of zinc a crystalline substance is produced; barium and calcium chlorides do not give any reaction.

No anhydride of the acid was obtained although an experiment was made as follows:—0·2 gram of the pure acid was heated in a metal-bath for 40 minutes at 300—320°, and then distilled by quickly raising the temperature: a small amount of carbonaceous residue was left, but almost the whole of the acid passed over as a slightly yellowish oily distillate, which condensed on the cooler parts of the tube and immediately solidified; it was purified by washing with a small quantity of ether, and a melting point taken, which was found to be 170—172°; metaphenylenediacetic acid melts

at 170°, and it is therefore clear that no anhydride had been formed.

Para-xylylene Cyanide, $C_6H_4(CH_2{\cdot}CN)_2$.

15 grams of para-xylylene bromide are dissolved in alcohol, and 8 grams of potassium cyanide dissolved in as little water as possible are added to the solution; no reaction takes place at first, but on heating the mixture double decomposition commences, a large quantity of a bright-yellow flocculent substance separating; this is, however, not para-xylylene cyanide, but a resinous compound formed by some more complicated secondary reaction: after boiling on the water-bath with reflux condenser until the penetrating odour of the bromide is no longer perceptible, the alcohol is distilled off and water added to the residue, when the cyanide is precipitated as a dirty-white solid. On shaking with ether, it is dissolved while the insoluble resinous impurities are left; after drying, the ether is evaporated and the para-xylylene cyanide is obtained crystallised on the sides of the flask.

It may be purified by redissolving it in ether, boiling with a little animal charcoal, filtering, and allowing the filtrate to evaporate slowly: by this means well-defined crystals are obtained which after recrystallisation are quite pure. On analysis, the following results were obtained:—

I. 0·1690 gram substance gave 0·4755 gram CO_2 and 0·0820 gram H_2O.

II. 0·12425 gram substance gave 19·7 c.c. Nitrogen. Bar. 718 mm. T = 7°.

	Calculated for $C_{10}H_8N_2$.	Found. I.	Found. II.
C	76·90 per cent.	76·73	—
H.....	5·13 „	5·39	—
N.....	17·95 „	—	18·16 per cent.

Para-xylylene cyanide is a colourless substance which crystallises in long three-sided prisms and melts at 96°; in whatever manner the conditions are varied, it seems impossible to avoid the formation of a large amount of the yellow resinous substance alluded to above; the yield of cyanide is, therefore, a poor one, being only about 50 per cent. of the theoretical.

Paraphenylenediacetic Acid, $C_6H_4(CH_2{\cdot}COOH)_2$.

When the preceding compound is hydrolysed, paraphenylenediacetic acid is obtained; for its preparation, 2 grams of the cyanide

were added to an excess of the calculated quantity of potash dissolved in methyl alcohol, and boiled on the water-bath with reflux condenser, until no further evolution of ammonia could be observed.

After evaporating the alcohol, the residue was taken up with water and dilute sulphuric acid until the solution showed a strongly acid reaction; paraphenylenediacetic acid was thus partially precipitated together with a small quantity of brown impurity; the whole was shaken out well with ether, when the acid dissolved, leaving most of the impurities. The ethereal solution was dried and the product obtained as a crystalline crust when the ether was distilled off; the yield was almost theoretical. To purify the acid, it was dissolved in alcohol, boiled with a little animal charcoal, the filtered solution evaporated to dryness on the water-bath, and the residue twice recrystallised from water containing a trace of alcohol. Para-phenylenediacetic acid is thus obtained in fine, colourless needles, which are very readily soluble in alcohol, far less so in water or ether, and melt at 240—241°. The analysis gave the following results:—

0·1730 gram substance gave 0·3920 gram CO_2 and 0·08850 gram H_2O.

	Calculated for $C_{10}H_{10}O_4$.	Found.
C	61·86 per cent.	61·80 per cent.
H	5·15 „	5·46 „
O	32·99 „	32·74 „

The silver salt is precipitated on adding nitrate of silver to a neutral solution of the ammonium salt as a white amorphous mass; it was collected, well washed with water, and dried, first on a porous plate, then at 100°, and analysed with the following result:—

0·2805 gram substance gave 0·1473 gram silver.

	Calculated for $C_{10}H_8Ag_2O_4$.	Found.
Ag	52·8 per cent.	52·6 per cent.

Paraphenylenediacetic acid is not converted into its anhydride even on heating at 300—320° for half an hour, since, by quickly raising the temperature, a product distils over which after washing with a little ether showed the same melting point as the original acid.

Note on the Preparation of Isophthalic Acid.

Meta-xylylenediethyl Ether, $C_6H_4(CH_2OC_2H_5)_2$.

The preparation of isophthalic acid by the oxidation of meta-xylene with potassium dichromate and dilute sulphuric acid (Fittig, Velguth,

Annalen, **148**, 11), is known to be very tedious owing to the extreme stability of this hydrocarbon, the greater portion of which remains unchanged even after continued boiling for days together. The following method was therefore worked out and found to give excellent results: meta-xylene is treated with the requisite quantity (2 mols.) of bromine at 125°, and the dibromide formed, without purification, is boiled with alcoholic potash, and thus converted into meta-xylylene diethyl ether. When this is treated with potassium dichromate and sulphuric acid, a quantitative yield of isophthalic acid is obtained; the ether was, however, first prepared in the pure state and investigated a little more closely; for this purpose pure meta-xylylene bromide was boiled for six hours with a solution of alcoholic potash which contained twice the calculated quantity of alkali, water was then added, and the oil which settled to the bottom separated from the aqueous solution, dissolved in ether, and allowed to stand over calcium chloride; after distilling off the ether, the product remained as a dark-brown oil which was found still to contain bromine, either owing to the presence of a trace of undecomposed meta-xylylene bromide, or of an intermediate compound having the formula $C_6H_4Br\cdot CH_2\cdot OC_2H_5$. It was therefore treated with zinc-dust and acetic acid, and the ether, thus freed completely from bromine, was isolated in the usual manner, and submitted to fractional distillation, when almost the whole distilled over between 235° and 255°; this process was twice repeated and meta-xylylene diethyl ether obtained in the pure state in the form of a colourless, mobile, pleasant-smelling oil; it was analysed with the following results:—

0·1392 gram substance gave 0·3805 gram CO_2 and 0·1153 gram H_2O.

	Calculated for $C_{12}H_{18}O_2$.	Found.
C	74·23 per cent.	74·53 per cent.
H	9·28 „	9·19 „
O	16·49 „	16·28 „

This compound boils at 246—247° (712 mm. pressure, uncorr.), and does not solidify even when cooled to 0°; it is isomeric with the ortho-derivative prepared by Leser (*Ber.*, **17**, 1825), which boils at 247—249° (720 mm. pressure).

Of course, when this ether is required for the preparation of isophthalic acid, it is quite unnecessary to purify it, the crude product of the action of alcoholic potash on the xylylene bromide is mixed directly with an excess of potassium dichromate in a large flask and sulphuric acid added; the reaction is very energetic and great heat is evolved, so that in working with large quantities it is advisable to add the acid very slowly or the mixture will be apt to froth over.

When the oxidation is completed, which is the case in a very short time, the isophthalic acid seen as a white sandy powder on the bottom of the flask is collected and washed with water; it is, however, very difficult to get rid of the last traces of the green mother-liquor, and to obtain the product quite pure, it is dissolved in sodium carbonate, and the filtered solution acidified with sulphuric acid. After washing the precipitated isophthalic acid and drying it at 100°, an analysis was made with the following result:—

0·1477 gram substance gave 0·3128 gram CO_2 and 0·0500 gram H_2O.

	Calculated for $C_8H_6O_4$.	Found.
C	57·77 per cent.	57·75 per cent.
H	3·61 ,,	3·76 ,,
O	38·62 ,,	38·49 ,,

In this way, an almost theoretical yield of isophthalic acid can be obtained from meta-xylene with comparative ease and in a short time, whereas by the old method, several days were required to prepare a few grams.

This work was carried out in the laboratory of Professor A. v. Baeyer in Munich, and, before closing, I desire to express my gratitude for the kindness which was invariably shown to me, and for the interest which he took in this research.

III.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. X.—*The Interaction of Zinc and Sulphuric Acid.*

By M. M. Pattison Muir, M.A., and R. H. Adie, B.A., Scholar of Trinity College, Cambridge.

1. In 1830 De la Rive examined the action which occurs between zinc and aqueous solutions of sulphuric acid (*Pogg. Ann.*, **19**, 221). He employed both commercial and redistilled zinc, and measured the times required for the production of equal volumes of hydrogen from acids of different concentrations. De la Rive found that the change proceeded much more rapidly with commercial than with redistilled

zinc; he also found that the most rapid action occurred when commercial zinc interacted with an acid solution containing about 30 per cent. H_2SO_4. De la Rive added known quantities of tin, lead, copper, and iron, respectively, to molten redistilled zinc, and found that the rates of action of the products with sulphuric acid solutions were greater than the rate of action of redistilled zinc. Finally, De la Rive proved that the solution of sulphuric acid which showed maximum electrical conductivity interacted most rapidly with commercial zinc, and with redistilled zinc to which a few per cent. of iron had been added. De la Rive concluded that the interaction between pure zinc and dilute sulphuric acid is probably a direct chemical change, but that with ordinary commercial zinc the action is chiefly electrochemical.

In the seventh series of his *Experimental Researches* (pars. 863 *et seq.*), Faraday proved that a plate of amalgamated zinc remained unchanged in sulphuric acid, to which 30 parts of water had been added, while a similar plate in the same acid put in contact with a plate of platinum lost 5·2 per cent. of its weight.

These experiments conducted by De la Rive and Faraday showed that the interaction which occurs between zinc and dilute sulphuric acid is to some extent at least an electrolytic action.

2. It is well known that hydrogen is not the only gaseous product of the interaction of dilute sulphuric acid and ordinary zinc. Everyday experience in the laboratory proves that both sulphur dioxide and sulphuretted hydrogen are often produced in the reaction in question. We have made a fairly complete qualitative examination of this interaction, and have found it to be one of great complexity.

About 10 grams of zinc were used in each experiment, and usually about 50 c.c. of the acid. The reactions proceeded in small flasks, each of which was connected by a T-tube with a flask containing a dilute aqueous solution of iodic acid mixed with a very little starch-paste, and also with a flask containing a dilute solution of silver nitrate to which excess of ammonia had been added. Exit-tubes from these flasks communicated with a water-pump; a current of air could thus be sucked through the whole apparatus, and traces of gases produced in the interactions could be swept out from the reaction-flask into the testing-flasks.

Those experiments wherein the reaction was allowed to proceed for long periods, sometimes extending to three weeks, were conducted in small flasks which were not connected with testing-flasks; at the end of the allotted time a rapid current of well-washed carbon dioxide was swept through the liquids in the flasks and the escaping gas was bubbled through the testing solutions.

The higher temperatures were maintained by heating the flasks in

baths of zinc chloride: for our purposes, it was unnecessary to attempt to regulate the temperatures within a few degrees. The specimens of zinc employed were (1) "redistilled zinc," (2) "pure rod zinc," (3) "pure zinc foil," (4) "commercial granulated zinc," the chief impurities in which were lead, iron, arsenic, and traces of cadmium, (5) "platinised zinc foil," and (6) "approximately pure zinc," prepared by us by dissolving "pure redistilled zinc" in pure very dilute sulphuric acid, saturating with sulphuretted hydrogen, boiling, filtering, electrolysing (after complete removal of H_2S), digesting the zinc thus obtained with a slightly warm aqueous solution of recrystallised "pure zinc sulphate," redissolving in pure dilute sulphuric acid, electrolysing, &c., and repeating the series of operations a third time.

The sulphuric acid employed was that sold as "pure redistilled," diluted with measured quantities of water. What is hereafter called "approximately pure H_2SO_4" was prepared by redistilling the "pure redistilled" acid, collecting the middle portion of the distillate, repeating this process, then freezing out the H_2SO_4, and pouring off the remaining liquid.

The concentrations of the various acids used are represented by formulæ, but these are to be regarded merely as approximate representations of the ratio of H_2SO_4 to H_2O in the liquids. The concentration varied from H_2SO_4 to $H_2SO_4,100H_2O$.

No attempts were made to measure the quantities of the different products of the reactions. When a blue colour in the iodic acid and starch test-liquid, or a brown colour in the silver nitrate test-liquid, appeared only after the current of air or carbon dioxide had swept through the apparatus for 30 minutes, we note the result as "a trace" of SO_2, or SH_2, as the case may be. Production of a deep-blue colour, or a brown-black precipitate, immediately the first bubbles of gas came into contact with the testing liquid, is noted as "abundance" of SO_2 (or SH_2). To save space and frequent repetition we have adopted the following letters for indicating (very roughly it is to be remembered) the results of the experiments:—

t.	*l.*	*m.*	*a.*
Trace.	A little.	Moderate quantity.	Abundance.

Statements are made in the sequel regarding the appearance of hydrogen: when the acid used was concentrated and the changes proceeded very slowly, the presence of hydrogen among the products was proved by continually passing a rapid current of carbon dioxide through the reaction-flask, and allowing the escaping gas to bubble through potash solution into a tube filled with the same solution, and testing the gas which collected in this tube.

Statements are also made in the sequel regarding the solid matter

formed in the reaction-flasks: this solid was proved to be free from zinc sulphide by collecting it on glass-wool filters, washing with sulphuric acid, thoroughly drying on a porous tile, and then decomposing it by fairly concentrated warm sulphuric acid in a flask connected with testing-flasks as already described. Direct experiments proved that zinc sulphide is decomposed by moderately dilute warm sulphuric acid, with formation of sulphur dioxide, sulphuretted hydrogen, and sulphur; the absence of these three substances was taken as evidence that the solid examined was free from zinc sulphide. Traces of sulphur were detected by warming the solid products of the reaction with carbon bisulphide, decanting, and evaporating the bisulphide.

The experiments, which were performed in duplicate, were always stopped when some zinc remained undissolved.

The following formulæ approximately represent the concentrations of the acids used; each acid is distinguished by a letter or number.

Letter.....	AA.	A.	B.
Concentration of acid..	H_2SO_4	$9H_2SO_4,H_2O$	$7H_2SO_4,2H_2O$

Letter.....	C.	D.
Concentration of acid..	$7H_2SO_4,4H_2O$	$7H_2SO_4,6H_2O$.

Number....	1.	2.	3.	4.
Concen. of acid....	H_2SO_4,H_2O	$H_2SO_4,2H_2O$	$H_2SO_4,3H_2O$	$H_2SO_4,4H_2O$;

and so on, the number n representing an acid of concentration H_2SO_4,nH_2O.

The following letters indicate roughly the quantity of the gas produced: *t*, trace; *l*, a little; *m*, moderate; *a*, abundance. The lines — — — indicate the absence of SO_2, SH_2, or S; these three bodies are always enumerated in this order; thus *t* — — means "a trace of sulphur dioxide, sulphuretted hydrogen and sulphur absent."

3. The following tables embody the greater number of our results:—

Products obtained by using Commercial Granulated Zinc and Acids of various concentrations.

Temperature	0°.			20°.			100°.			160°.		
Concentr. of acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A				*t*	—	—	*m*	—	—	*a*	*l*	*t*
B				*l*	*l*	—	*a*	*t*	*t*			
C				*l*	*l*	—						
D				*l*	*l*	—	*l*	*l*	*t*	\		
1							*m*	*l*	*t*			
2				—	*t*	—	—	—	—	*t*	*a*	—
4							—	*t*	—	*l*	*t*	—
6	—	*l*	—									
7	*l*	*l*	—	*m*	*m*	—						
8	*l*	*l*	—				—	*m*	—			
9	*l*	*l*	—									
10	*l*	*l*	—									
11	*m*	*m*	—									
12	*m*	*m*	—				*l*	*a*	—			
13	*l*	*m*	—									
16				*a*	*a*	—						
25	*t*	*m*	—				*t*	*a*	—			
50	—	*l*	—									
100	*t*	*l*	—									

Products obtained by using Redistilled Granulated Zinc and Acids of various concentrations.

Temperature	0°.			110°.			160°.		
Concentr. of Acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A							*a*	*t*	*t*
1							*a*	*a*	*a*
2	—	—	—						
3	—	—	—						
4				*l*	*l*	—			
5	—	—	—						
7	—	—	—	*t*	*l*	—			
9	—	*t*	—						
11	*t*	*t*	—						
12				*t*	*t*	—			
13	—	*t*	—						
16	—	*t*	—						
25	—	—	—						
50	—	—	—						

Products obtained by using Platinised Zinc Foil and Acids of various concentrations.

Temperature	0°.			20°.			100°.			150°.			160—170°.			B. p. of acid.		
Concentr. of acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A				*m*	—	—	*m*	—	—				*m*	*l*	*m*	*a*	*m*	—
B							*l*	*t*	*t*				*m*	*m*	*m*	*a*	*a*	—
C							*m*	—	—	*a*	*l*	—	*a*	*m*	*m*	*m*	*a*	—
1				*t*(?)	*t*(?)	—	*m*	—	—	*l*	*m*	*m*	*m*	*m*	*m*	*m*	*a*	—
2							*l*	*l*	—	*m*	*m*	*t*	*m*	*m*	—			
3	—	—	—															
4				—	—	—	—	*t*(?)	—									
5	—	—	—															
7	—	*t*	—	—	*t*(?)	—	—	—	—									
9	*t*	*l*	—															
11	*t*	*l*	—															
13	—	*l*	—															
16	*t*	*t*	—															
25	—	*t*	—	—	*t*	—	—	—	—									
50	—	—	—															
100				—	*t*	—												

Products obtained by using "Approximately Pure" Zinc and Acids of various concentrations.

Temperature	15—18°.			110—112°.			135°.			145°.			160°.			200—250°.		
Concentr. of acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A	*t*	—	—				*l*	—	—	*a*	—	—				*a*	*t*	—
B													*m*	*t*	*t*			
2													*m*	*m*	—			
12				—	*t*	—												

Products obtained by using Pure Rod Zinc and Acids of various concentrations.

Temperature	110°.			160°.			B. p. of acid.		
Concentr. of acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A				*a*	*t*	*m*	*l*	*t*	—
B				*a*	*a*	*a*			
C				*a*	*a*	*a*			
D				*a*	*a*	*t*			
1				*a*	*a*	*t*			
2				*a*	*a*	*t*			
3				*l*	*l*	—			
4				*l*	*l*	—			
8	*t*	*t*	—						
12*	—	*l*	—						

* Acid of this strength gives only hydrogen at 85°.

Products obtained by using Pure Zinc Foil and Acids of various concentrations.

Temperature	20°.			100°.			160°.			B. p. of acid.		
Concentr. of acid.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.	SO_2,	SH_2,	S.
A	—	—	—	*m*	—	—	*a*	*l*	—			
B	—	—	—									
1	—	—	—	*l*	—	—				*l*	*m*	*t*
2	—	—	—	*l*	*l*	—						
3	—	—	—									
4	—	—	—									
5	—	—	—									

4. We think it may be safely asserted that hydrogen was produced in all the reactions. Direct proof of the presence of hydrogen was sought for and found in the cases of the acids H_2SO_4,H_2O at the ordinary temperature, $9H_2SO_4,H_2O$ at 100°, $7H_2SO_4,2H_2O$ at 100°, and platinised zinc with $7H_2SO_4,2H_2O$ at 150—180°, at which temperature sulphur was freely produced.

The only solid product of the interaction is zinc sulphate. This was proved for acid of very varying concentrations and at different temperatures; for $9H_2SO_4,H_2O$ at 180°, $7H_2SO_4,2H_2O$ at 100°, and $H_2SO_4,3H_2O$, $H_2SO_4,4H_2O$, and $H_2SO_4,6H_2O$ at ordinary temperatures.

5. The results of our experiments, when regarded broadly, establish a similarity between the interaction of sulphuric acid with approximately pure zinc and with commercial zinc. But at the same

time there are differences. Thus the results show that as the zinc becomes purer the quantities of sulphur dioxide and sulphuretted hydrogen, particularly the latter, produced at the ordinary temperature (12—18°) become markedly less, whether the acid be concentrated or dilute; when the acid is so dilute as H_2SO_4,10 or $12H_2O$, hydrogen is almost the sole gaseous product, even at temperatures up to the boiling point of the acid used. When approximately pure zinc is employed and the temperature is high (160° or so), dilution of the acid is accompanied by diminution both of sulphur dioxide and sulphuretted hydrogen; but when commercial zinc is used, the sulphur dioxide diminishes more than the sulphuretted hydrogen; when commercial zinc was used, however, small quantities of sulphuretted hydrogen were indeed obtained with every acid examined, even with H_2SO_4,$100H_2O$, and at temperatures varying from the boiling point of the acid to 0°.

Platinised zinc foil behaves on the whole similarly to commercial zinc; sulphur dioxide and sulphuretted hydrogen are produced at very varying temperatures, and with almost every acid examined. When the acid is fairly concentrated, sulphur dioxide begins to be produced at a temperature lower than that at which sulphuretted hydrogen appears, both in the case of platinised foil and commercial zinc; when the acids are dilute, the tendency in the case of platinised zinc foil is to produce sulphuretted hydrogen more freely than sulphur dioxide.

It is somewhat remarkable that scarcely any sulphur dioxide or sulphuretted hydrogen should be produced when commercial zinc and acid, approximately of the concentration H_2SO_4,$2H_2O$, interact at 100°, but that at 165° abundance of sulphuretted hydrogen accompanied by a little sulphur dioxide should be formed, and that at 180° torrents of the former gas nearly free from sulphur dioxide should be evolved. In connection with this result it is of interest to note that "approximately pure" zinc, interacting with acid of the same concentration as the above (H_2SO_4,$2H_2O$) at 160°, produces quantities of both the gases in question.

6. The production of sulphur requires a little examination. The conditions under which sulphur appeared are noted in the table on p. 55.

In the experiments with platinised foil, sulphur disappeared again at 210—220°, and SH_2 increased very much.

Sulphur did not appear in any other experiment with "approximately pure zinc;" the other acids examined were H_2SO_4 and H_2SO_4,$2H_2O$.

Sulphur is produced neither at low temperatures, nor with acids less concentrated than H_2SO_4,$2H_2O$; the formation of sulphur is always accompanied by the evolution of sulphur dioxide and sulphuretted hydrogen, but the quantity of the latter gas is sometimes extremely

Kind of zinc.	Concentration of acid.	Temp.	Remarks.
"Pure rod zinc".....	Approx. H_2SO_4	165°	Very little S; plenty of SO_2; merest trace of SH_2.
"	$9H_2SO_4,H_2O$	165	Decided S; plenty of SO_2; merest trace of SH_2.
"	$7H_2SO_4,2H_2O$	165	Decided S; plenty of SO_2 and SH_2.
"	$7H_2SO_4,4H_2O$	165	Decided S; much SO_2; little SH_2.
"	$7H_2SO_4,6H_2O$	165	Little S; much SO_2 and SH_2.
"	$H_2SO_4,2H_2O$	165	Trace of S; much SO_2 and SH_2.
"Pure zinc foil"	H_2SO_4,H_2O	190	Distinct S; fair quantities of SO_2 and SH_2.
"Commercial granulated zinc"	$9H_2SO_4,H_2O$	165	Little S; much SO_2; little SH_2.
"	$7H_2SO_4,2H_2O$	100	Little S; much SO_2; very little SH_2.
"	$7H_2SO_4,6H_2O$	100	Little S; little SO_2 and SH_2.
"	H_2SO_4,H_2O	100	Trace of S; fair quantity of SO_2; little SH_2.
"Platinised foil"	$7H_2SO_4,2H_2O$	175—185	Much S; very much SO_2; little SH_2.
"	$7H_2SO_4,4H_2O$	175—180	Much S; much SO_2; little SH_2.
"	$7H_2SO_4,6H_2O$	175	" "
"	H_2SO_4,H_2O	170	" "
"	$H_2SO_4,2H_2O$	130	Trace of S; much SO_2; fair quantity of SH_2.
"Approximately pure zinc"	$7H_2SO_4,2H_2O$	160°	Small quantity of S; quantity of SO_2; trace of SH_2.

small. When "approximately pure" zinc and sulphuric acid are used, there is scarcely any separation of sulphur; with platinised foil, on the other hand, sulphur is formed in large quantities. The sulphur can scarcely be a product of the interaction of sulphur dioxide and sulphuretted hydrogen, else we should expect to find it generally accompanying these gases; nor can it always be produced by the reducing action of the nascent hydrogen on either the sulphur dioxide or sulphuretted hydrogen, because these gases are so frequently found at moderate temperatures unaccompanied by sulphur. It may be that the formation of sulphur is sometimes to be traced to the mutual action of sulphuretted hydrogen and hot concentrated sulphuric acid. This supposition would account for the preponderance of sulphur dioxide over sulphuretted hydrogen when the acid is concentrated, and for the increase in the quantity of the latter gas as the acid becomes more dilute: for the sulphuretted hydrogen supposed to be formed when the acid is concentrated would be decomposed by

reacting with the hot acid, but would escape unchanged when the acid becomes more dilute. The fact that the cessation in the production of sulphur is accompanied by a marked increase in the quantity of sulphuretted hydrogen in the reaction of platinised foil with concentrated acids, is also in keeping with this supposition. The non-production of sulphur when "approximately pure" zinc is used supports the view that some of the sulphur is formed in secondary reactions between the gaseous products, or between these and the acid, rather than in the direct interaction of the metal and acid.

The sulphur produced was soluble in carbon bisulphide.

7. Increase of the mass of the zinc relatively to that of the acid does not produce any regular and definite effect on the nature or quantities of the gaseous products of the change. This is shown by the tabulated results given on p. 57.

8. The interaction between zinc and sulphuric acid evidently differs considerably from the interaction between copper and sulphuric acid (see Pickering, Trans., 1878, 112). The latter change proceeds in two definitely marked stages expressible by the equations—

$$(1.)\ 5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$$
$$(2.)\ Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Hydrogen is not obtained in the reaction between copper and sulphuric acid nor is sulphuretted hydrogen evolved; the sulphur dioxide produced is most probably the result of secondary reactions occurring between the acid and the cuprous sulphide formed. In the interaction between zinc and sulphuric acid, on the other hand, hydrogen appears to be always produced; both sulphuretted hydrogen and sulphur dioxide are very frequently formed, and the production of these gases cannot be traced to a secondary reaction between the acid and zinc sulphide formed in the primary change; the entire interaction is more irregular than that between copper and sulphuric acid.

The dependence of the production of large quantities of sulphur dioxide and sulphuretted hydrogen in the interaction between zinc and sulphuric acid on the temperature and the concentration of the acid indicates, we think, that the formation of these gases is not to be altogether ascribed to the reducing action of nascent hydrogen on the acid. This view is confirmed by the fact that variations in the mass of the zinc employed, and hence in the quantity of hydrogen produced in a specified time, do not exert any marked or regular effect on the nature of the change. The behaviour of commercial zinc with acid of the concentration $H_2SO_4,2H_2O$, and of approximately pure zinc with the same acid, also confirms this supposition: in the case of commercial zinc, very little sulphur dioxide or sulphuretted hydrogen is

Various Zincs with Acids of different concentrations; 50 c.c. acid used in each case.

Acid.	Weight of zinc used.	Approximate temp. of appearance of		Remarks.
		SO_2.	SH_2.	
	grams.	°	°	
I. *Pure rod zinc*—				
$7H_2SO_4,2H_2O$	7	144—146	135—137	Little SH_2 even at 150°.
	14	150	137	" "
$H_2SO_4,2H_2O$	7	150—155	145	Plenty of both gases at 155°.
	14	135—140	130—135	
II. *Pure zinc foil*—				
$7H_2SO_4,2H_2O$	7	120—125	90—95	
	14	105—110	70—75	
	21	105—110	70—75	
$7H_2SO_4,6H_2O$	7	125—130	105—110	
	14	130—135	100	
	21	115—120	85	
$H_2SO_4,2H_2O$	7	140—145	130	
	14	145—150	135	
$H_2SO_4,4H_2O$	7	135—140	120—125	
	14	140	125	
	21	135—140	120—125	
III. *Redistilled zinc*—				
$H_2SO_4,2H_2O$	3·5	150	120	SO_2 rapidly at once; SH_2 slowly increasing.
	5	150	130—135	
	7	130—135	130—135	
	14	140—145	125—130	
	28	140	135—140	
	35	135	125—130	
IV. *Commercial granulated zinc*—				
$H_2SO_4,2H_2O$	7	140—145	135—140	Not much SH_2 till 145°.
	14	140—145	125—135	Plenty SH_2 at 150°.
V. *Platinised zinc foil*—				
$H_2SO_4,2H_2O$	7	110	70—80	Not much SO_2 till 130°, and SH_2 till 90°.
	14	105	85—90	

formed at 100°; at 165° both gases are produced freely; and at 180° the latter gas is evolved in very large quantity; in the case of approximately pure zinc, both gases are produced in quantity at 165°. Moreover, if the gases in question were altogether secondary products of the reduction of sulphuric acid by the hydrogen evolved in the primary change, we should expect to find them formed as freely when

the former zinc is used as when commercial zinc is employed; but this supposition is not confirmed by experiment. We are inclined to think that the interaction between approximately pure zinc and acid is chiefly a direct chemical interaction, and that the products of the reactions with the less pure zincs are largely due to the occurrence of secondary electrolytic changes. With pure, or almost pure, zinc and dilute acid (say H_2SO_4,12 to $15H_2O$), hydrogen and zinc sulphate are the only products of the reaction; with the same zinc and concentrated acids (say H_2SO_4,H_2O to H_2SO_4) the chief gaseous product is sulphur dioxide, and sulphuretted hydrogen is also produced at higher temperatures; with an acid of intermediate concentration (in our experiments with H_2SO_4,$2H_2O$) both compounds of sulphur are formed in considerable quantities at fairly high temperatures (160°). But the results of our experiments make it certain that whether the zinc be pure or commercial, the concentration of the acid used plays a most important part in the chemical change; hence it is probable that the bodies actually interacting are numerous, and that the reactions are much more complex than can well be represented in any series of equations which can at present be devised. It seems to us that the chemical change which occurs is to be ascribed to the interaction of the zinc with various molecular aggregates of H_2SO_4 and H_2O, probably also of SO_3 and H_2O, or of H_2SO_4, SO_3, and H_2O; and that the compositions of these aggregates probably vary with variations in the concentration of the acid used and with variations of temperature.

The results of experiments on the electrolysis and electrolytic conductivity of sulphuric acid* establish a close resemblance between the electrochemical behaviour of this acid and its chemical behaviour as described in this paper.

* Wiedemann, *Die Lehre von der Elektricität*, **2**, 538; also F. Kohlrausch, *Ann. Phys. Chem.*, **26**, 206; also Ostwald, *Phil. Mag.*, August 1886, and other places; also Gladstone and Tribe, this Journal, Trans. for 1879, 177.

IV.—*The Dehydration of Metallic Hydroxides by Heat, with special reference to the Polymerisation of the Oxides, and to the Periodic Law.*

By Professor T. Carnelley, D.Sc., and Dr. James Walker, University College, Dundee.

Oxygen being a much more fusible and volatile element than chlorine it would, *à priori*, be supposed that the oxides of the elements would also be more fusible and volatile than the corresponding chlorides. Prof. Louis Henry, however, in a most interesting paper (*Phil. Mag.* [5], **20**, 81; *Annales de la Soc. Sci. de Brux.*, 1879) has drawn special attention to the fact that, with but comparatively few exceptions, chiefly those of negative elements, the oxides are by far the less fusible and volatile of the two classes of compounds, and that unlike their chlorides they are distinguished by their comparative fixity and infusibility.

The chlorides and oxides are generally represented by comparable formulæ, but whereas the formulæ usually assigned to the chlorides have been deduced from the determination of their vapour-density, those attributed to the oxides depend, with very few exceptions, solely on analytical determinations, and they are therefore merely empirical, and have no claim to a molecular signification. Henry, for numerous very cogent reasons, concludes that most of the known oxides of the elements, and notably the metallic oxides, are *polymerides* $n(RO_x)$ of the unknown true oxides RO_x, corresponding to the chlorides RCl_{2x}. Now the fusibility and volatility of a compound are in a very great measure directly dependent on the molecular weight, and he would hence account for the almost general infusibility and fixity of the oxides by their being in most cases polymerides, with molecular weights much higher than those represented by the empirical formulæ usually assigned to them.

The object of the present investigation was: first, to ascertain whether some light could be thrown on the above question of the polymerisation of the metallic oxides from the change in composition of the hydroxides on heating at regularly increasing temperatures; and second, to determine the minimum temperature of complete dehydration of the metallic hydroxides, with a view of ascertaining whether this temperature was a periodic function of the atomic weight of the positive element.

Wurtz, in 1863, showed that when a hydroxide is decomposed by heat, the chemical action is twofold: (1.) Dehydration, which may be partial or complete. (2.) Molecular condensation, resulting from two

or more molecules of the hydroxide entering into combination on the elimination of a part or the whole of the hydrogen of the hydroxide as water. It therefore follows that the compounds thus formed become more and more complex, in proportion to the extent of the dehydration.

By heating certain hydrates at regularly increasing temperatures, and determining the degree of dehydration thus produced, it seemed probable that data could be obtained for the construction of curves, which would indicate whether any compounds were formed intermediate between the normal hydrates and the corresponding oxides, and thus give some information in regard to the general phenomena occurring during the dehydration. The composition of these compounds, if formed, might also afford some clue to the true molecular weights of the oxides. Their existence could be recognised by observing when, for a considerable increase of temperature, little or no decrease in their weight took place.

The hydrates (or precipitated oxides) corresponding to the following were prepared:—

1. Ag_2O,
2. HgO,
3. Al_2O_3, In_2O_3, Tl_2O_3,
4. SiO_2, TiO_2, ZrO_2, SnO_2, CeO_2, PbO_2,
5. Sb_2O_3, Bi_2O_3,
6. Fe_2O_3, Co_2O_3, Ni_2O_3.

Many hydrates, such as those of calcium, barium, magnesium, zinc, cadmium, &c., absorb large quantities of carbonic anhydride from the air whilst drying, and therefore could not be employed. The moist oxides of silver and bismuth take up small quantities of carbonic anhydride.

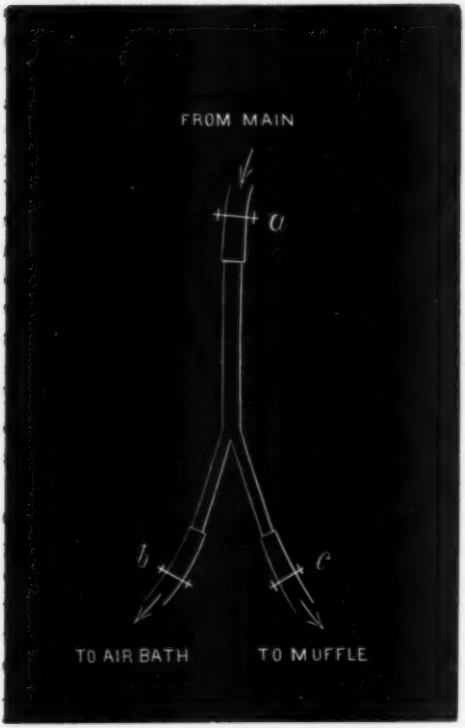
To obtain the hydrates as far as possible in the same state of aggregation, they were prepared under the same conditions, as nearly as the differences in the nature of the substances would allow. Solutions of mercuric chloride and silver nitrate were precipitated in the cold, with a slight excess of caustic soda solution. The cold solutions of aluminium sulphate, bismuth nitrate, antimony trichloride, ferric chloride, zirconium sulphate, thallic sulphate, indium chloride, and cerium sulphate were precipitated with ammonia. Anhydrous titanium tetrachloride was added gradually to cold aqueous ammonia. Sodium silicate and sodium stannate were precipitated with cold dilute hydrochloric acid. Cobalt chloride and nickel sulphate were precipitated with caustic potash, and the precipitate boiled to get rid of any basic salts. Well washed chlorine gas was then passed through the suspended oxides after cooling, until the liquid was thoroughly saturated,

and smelt strongly of chlorine even on long standing and repeated agitation. In the same way, chlorine was passed through a solution of lead acetate precipitated with sodium carbonate solution.

The hydrates (and oxides) obtained as above were washed with cold water, first by decantation, and afterwards on the filter, until the washings were quite neutral, and showed no trace of the acid contained in the salt precipitated or in the precipitant, as the case might be. After being partially air-dried on the filter, the hydrates were spread out on glass plates and allowed to dry in the air for at least 10 days before being used; as the drying proceeded, the substances were powdered as finely as possible. The silver precipitate was kept in the dark during the whole course of the investigation.

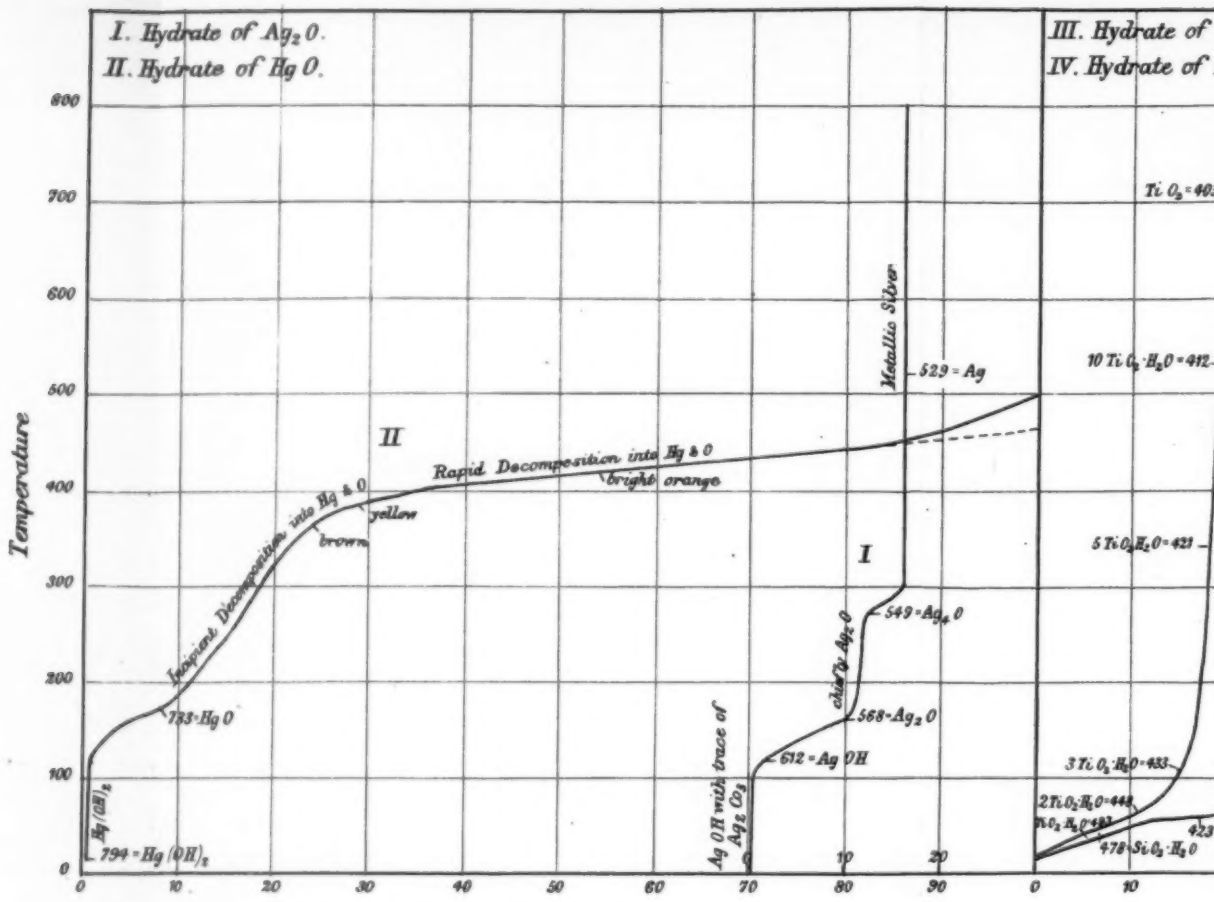
For determining the dehydrating action of heat on the hydroxides obtained as above, a small, double-walled copper air-bath with ordinary Bunsen lamp was employed. It was placed inside a draught-cupboard, the flue of which was stopped, so that the temperature inside the bath could be kept constant within less than a degree for several hours at a time, by occasionally regulating the gas pressure by means of the taps. The hydrates were contained in small porcelain crucibles, which were placed on a glass plate resting on a shelf in the middle of the bath. Hydrates of the same group of elements were always heated at the same time. The lowest temperature used was about 50°, and this was afterwards increased by about 10° at each heating. After about two hours' heating at any given temperature, the weight of the hydrates remained sensibly constant, consequently the crucibles were allowed to remain in the bath for fully two hours at each temperature, and were then removed to desiccators, cooled and weighed.

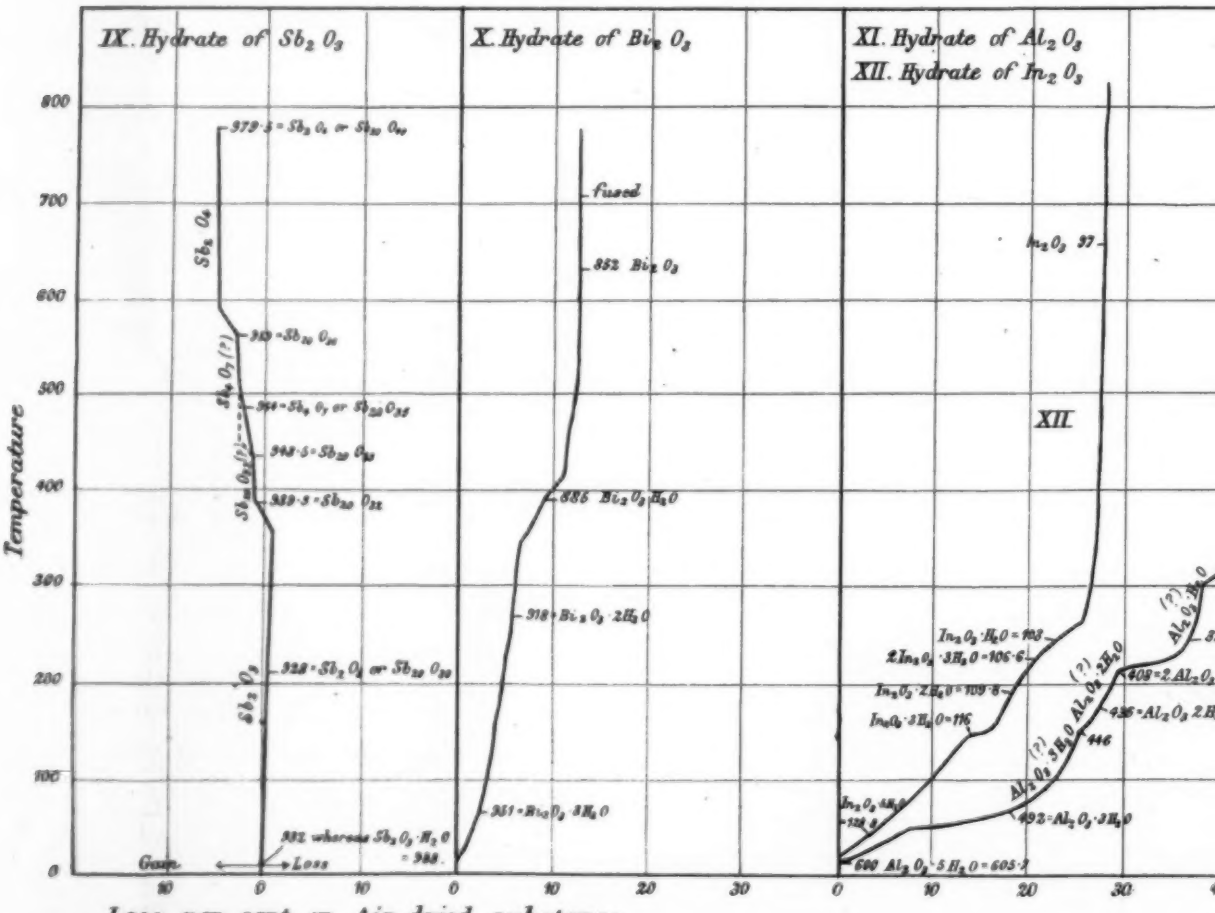
An ordinary mercury thermometer was used up to 300°, and its readings were not corrected, as all that was needed for the purposes of the investigation was that the temperature should increase by comparatively small and tolerably regular intervals. Above 300°, the melting points of different salts were used to measure the temperature; under these circumstances the crucibles were placed on an iron plate, resting on pieces of asbestos on the floor of a muffle furnace, with the walls of which it was not in contact. The mouth of the muffle was closed by an iron plate, in which was cut a hole for the introduction of a long, shallow, iron trough, containing the salts to be used as indicators. This trough could be slid in and out amongst the crucibles, and, when in the muffle, it rested on the iron plate. When the muffle had attained the correct temperature, the following arrangement was used to keep it constant:—An india-rubber tube from the gas main was connected with a Y-tube, and to the branches of the Y were attached other india-rubber tubes, one going to the muffle, and the other to the



small copper air-bath previously referred to. By means of the pinch-cocks *b* and *c*, the flow of gas could be so regulated, that when the muffle was at nearly the desired temperature the Bunsen flame under the air-bath was quite sensitive to a small movement of the pinchcock *a*, which could then be used to get the correct temperature. When this had been attained, the thermometer in the air-bath was read off, and kept by means of *a* at the same temperature during the whole heating. It was thus assumed that if the flow of gas was so regulated that the temperature of the air-bath remained constant, that of the muffle would remain constant also. The indications of the thermometer in the air-bath were checked several times in the course of each heating by means of the melting points of the salts heated in the muffle. Tests made with the salts showed that there was an almost uniform temperature prevailing at the different parts of the iron plates on which the crucibles rested. The following is a list of the salts employed as temperature indicators, together with their melting points as determined by one of us in a communication made to the Society some years ago. As the temperature of the muffle would

DIAGRAM SHOWING THE DEHYDRATIO


I. Hydrate of Ag_2O.
II. Hydrate of HgO.
III. Hydrate of
IV. Hydrate of
Temperature
Loss per cent. on Air-dried substance.
Metallic Silver
529 = Ag
549 = Ag_4O
568 = Ag_2O
612 = AgOH
733 = HgO
794 = $Hg(OH)_2$
Rapid Decomposition into Hg & O
bright orange
yellow
brown
Incipient Decomposition into Hg & O
Ag OH with trace of Ag_2CO_3
$Ti O_2$ = 40
10 $Ti O_2 \cdot H_2O$ = 412
5 $Ti O_2 \cdot H_2O$ = 421
3 $Ti O_2 \cdot H_2O$ = 433
2 $Ti O_2 \cdot H_2O$ = 448
$Ti O_2 \cdot H_2O$ = 482
423
478 $Si O_2 \cdot H_2O$



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YDRATION OF THE METALLIC HYDRATES BY HEAT.

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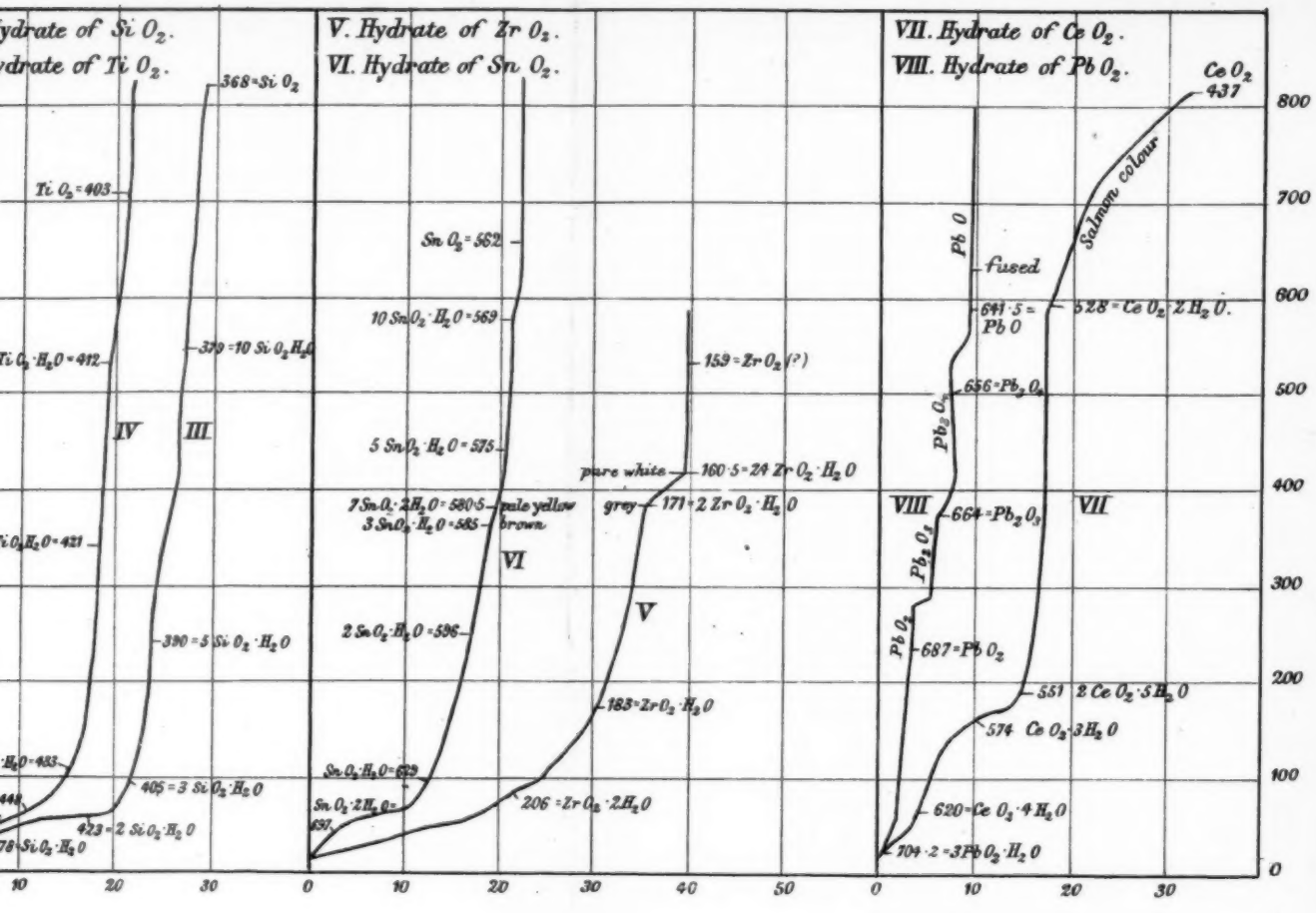
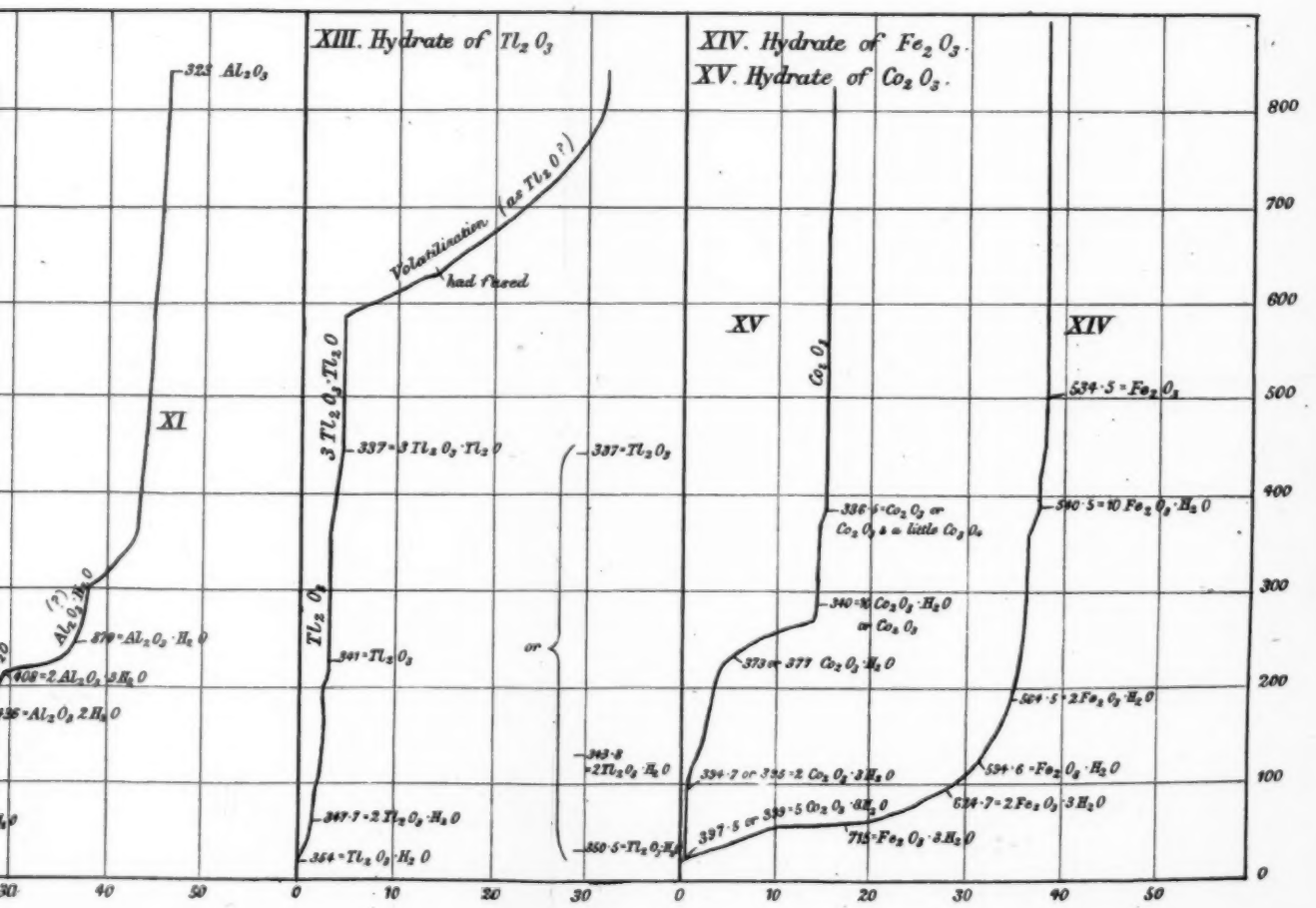

ydrate of Si O2.
ydrate of Ti O2.
V. Hydrate of Zr O2.
VI. Hydrate of Sn O2.
VII. Hydrate of Ce O2.
VIII. Hydrate of Pb O2.
Ti O2 = 403
368 = Si O2
379 = 10 Si O2 H2O
390 = 5 Si O2 · H2O
405 = 3 Si O2 · H2O
423 = 2 Si O2 · H2O
Sn O2 = 562
10 Sn O2 · H2O = 569
5 Sn O2 · H2O = 575
7 Sn O2 · 2H2O = 580·5
3 Sn O2 · H2O = 585
2 Sn O2 · H2O = 596
Sn O2 · H2O = 629
Sn O2 · 2H2O =
159 = Zr O2 (?)
pure white
160·5 = 24 Zr O2 · H2O
grey
171 = 2 Zr O2 · H2O
183 = Zr O2 · H2O
206 = Zr O2 · 2H2O
Ce O2
437
Salmon colour
Pb O
fused
641·5 = Pb O
528 = Ce O2 · 2 H2O.
656 = Pb3 O4
664 = Pb2 O3
687 = Pb O2
551 2 Ce O2 · 5 H2O
574 Ce O2 · 3 H2O
620 = Ce O2 · 4 H2O
704·2 = 3 Pb O2 · H2O
I
II
III
IV
V
VI
VII
VIII


323 Al2 O3
(?) Al2 O3 · H2O
879 = Al2 O3 · H2O
408 = 2 Al2 O3 · 3 H2O
XI
XIII. Hydrate of Tl2 O3
Volatilisation (as Tl2 O?)
had fused
3 Tl2 O3 · Tl2 O
337 = 3 Tl2 O3 · Tl2 O
337 = Tl2 O3
Tl2 O3
341 = Tl2 O3
or
343·8 = 2 Tl2 O3 · H2O
347·7 = 2 Tl2 O3 · H2O
354 = Tl2 O3 · H2O
350·5 = Tl2 O3 · H2O
XIV. Hydrate of Fe2 O3.
XV. Hydrate of Co2 O3.
XV
Co2 O3
XIV
534·5 = Fe2 O3
336·4 = Co2 O3 or
Co2 O3 & a little Co3 O4
340 = Co2 O3 · H2O
or Co2 O3
373 or 377 Co2 O3 · H2O
394·7 or 395 = 2 Co2 O3 · 3 H2O
397·5 or 399·5 Co2 O3 · 3H2O
540·5 = 10 Fe2 O3 · H2O
524·5 = 2 Fe2 O3 · H2O
534·6 = Fe2 O3 · H2O
524·7 = 2 Fe2 O3 · 3 H2O
715 = Fe2 O3 · 3 H2O

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always be a degree or two above that at which the salts melted, the round numbers given in the third column have been used instead of the melting points as determined.

Salt.	Melting point.	Temperature of muffle.
KNO_3	339° C.	say 340°
$KClO_3$	359	360
PbI_2	383	385
$Ba(ClO_3)_2$	414	415
TlI	439	440
$PbCl_2$	498	500
AgBr	527	530
$Ca(NO_3)_2$	561	565
KIO_4	582	585
NaI	628	630
Ag_2SO_4	654	655
NaBr	708	710
NaCl	772	775
Na_2CO_3	814	815

The crucibles and their contents were finally ignited over the blow-pipe.

The results obtained are shown in the following series of tables, in which Column I gives the temperature, Column II the weight of the substance after heating for at least two hours at that temperature, Column III the difference from the previous weighing calculated* for an increase of 10°, and Column IV the loss per cent. on the substance dried at about 15°.

The above results are represented graphically in Diagram I, in which the ordinates indicate temperature and the abscissæ the corresponding loss per cent. on the air-dried substance. The numbers affixed at certain points to the right-hand side of the curves give the composition of the hydrate at these positions, and represent the weight of the attached hydrate corresponding to the weight of the anhydrous oxide shown at a higher point in the curve. Thus, in Curve III the expression [$478 = SiO_2,H_2O$] indicates that at this point the hydrate had the composition SiO_2,H_2O, the number 478 being the weight in mgrms. of this hydrate, which on complete dehydration gave 368 mgrms. of anhydrous SiO_2. (N.B.—These numbers are taken from column II in the foregoing table.)

* This calculation was necessary, as the actual increase was not always the same, but varied from 10—13° for temperatures below 300°, and by greater and less regular intervals above that temperature.

I. Hydrate of Ag_2O (air-dried for six months).				II. Hydrate of HgO (air-dried for five months).			
I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.	I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.		°	mgrms.	mgrms.	
15	625·5	—	—	15	794·5	—	—
50	625·0	−0·1	0·08	50	793·5	−0·3	0·13
62	625·0	0	0·08	61	792·5	0·9	0·25
74	625·0	0	0·08	74	792·0	0·4	0·31
87	625·0	0	0·08	86	791·0	0·8	0·44
99	624·5	0·4	0·16	98	790·0	0·8	0·57
111	621·0	2·9	0·72	110	788·5	1·2	0·75
123	617·0	3·3	1·36	121	785·5	2·7	1·13
135	607·5	7·9	2·88	132	782·0	3·2	1·57
147	582·5	20·8	6·88	143	772·5	8·6	2·76
159	567·5	12·5	9·27	153	760·0	12·5	4·34
171	558·0	7·9	10·80	164	744·5	14·1	6·29
183	556·0	1·7	11·11	174	727·0	17·5	8·50
195	555·0	0·8	11·27	185	716·5	9·5	9·82
207	554·5	0·4	11·35	196	705·5	10·0	11·20
219	554·5	0	11·35	208	697·5	6·7	12·21
230	554·0	0·4	11·43	218	690·5	7·0	13·10
242	553·0	0·8	11·59	230	682·0	7·1	14·16
254	551·5	1·2	11·83	241	673·0	8·2	15·27
266	550·5	0·8	11·99	253	666·0	5·8	16·17
279	548·5	1·5	12·31	264	660·5	5·0	16·86
291	542·5	5·0	13·27	275	654·5	5·4	17·62

I. Hydrate of Ag_2O (air-dried for six months).				II. Hydrate of HgO (air-dried for five months).			
I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.	I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.		°	mgrms.	mgrms.	
340	528·0	−3·0	15·57	286	651·0	−3·2	18·06
360	528·0	0	15·57	298	646·0	4·2	18·69
385	528·0	0	15·57	340	620·0	6·0	21·84
415	528·5	+0·2	15·49	360	601·5	9·2	24·17
440	529·0	+0·2	15·41	385*	556·0	18·2	29·89
500	529	0	15·41	415	501·0	18·3	36·82
530	529	0	15·41	440†	144·0	142·8	81·75
565	529	0	15·41	500	0·5	24·0	99·9
585	529	0	15·41	530	0·5	0	99·9
630	529	0	15·41	565	0·5	0	99·9
655	529	0	15·41	585	1·0	+0·2	99·9
700	527	−0·4	15·83	630	1·0	0	99·9
Blowpipe	527	0	15·83	655	1·0	0	99·9
				710	1·0	0	99·9

* Colour changed from brown to yellow with white specks.
† Specks disappeared, and the whole turned bright orange.
N.B.—In these and all other cases the colour refers to the substance when *cold*.

III. Hydrate of SiO_2 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	516·0	—	—
51	459·5	−15·7	10·95
63	415·0	37·1	19·60
75	409·5	4·6	20·64
87	406·0	3·0	21·12
99	402·5	3·0	22·00
110	401·0	1·4	22·29
123	398·5	1·9	22·77
135	397·0	1·2	23·06
147	396·0	0·8	23·26
159	395·0	0·8	23·46
171	395·0	0	23·46
183	394·0	0·8	23·65
195	392·0	1·7	24·03
207	391·5	0·4	24·13
219	391·0	0·4	24·23
231	390·5	0·4	24·33
243	390·0	0·4	24·42
255	389·5	0·4	24·52
267	389·0	0·4	24·61
279	388·5	0·4	24·71
291	388·0	0·4	24·81
340	388·0	0	24·81

IV. Hydrate of TiO_2 (air-dried for 14 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	511·0	—	—
51	471·0	−11·1	7·83
63	452·0	15·8	11·55
75	446·0	5·0	12·72
87	440·5	4·6	13·80
99	436·0	3·7	14·68
110	433·5	2·3	15·17
123	430·5	2·3	15·75
135	429·0	1·2	16·05
147	427·5	1·2	16·34
159	426·5	0·8	16·54
171	426·5	0	16·54
183	425·5	0·8	16·73
195	425·0	0·4	16·83
207	425·0	0	16·83
219	425·0	0	16·83
231	424·5	0·4	16·93
243	424·0	0·4	17·03
255	423·5	0·4	17·13
267	423·0	0·4	17·22
279	422·5	0·4	17·32
291	422·5	0	17·32
340	421·0	0·3	17·62

III. Hydrate of SiO_2 (air-dried for five months).				IV. Hydrate of TiO_2 (air-dried for 14 days).			
I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.	I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.		°	mgrms.	mgrms.	
360	385·5	−1·2	25·29	360	420·0	−0·5	17·81
385	382·5	1·2	25·87	385	417·5	1·0	18·3
415	381·0	0·5	26·16	415	417·0	0·2	18·4
440	380·0	0·4	26·36	440	416·0	0·4	18·6
500	380·0	0	26·36	500	413·0	0·5	19·18
530	379·5	0·2	26·46	530	412·0	0·3	19·37
565	378·5	0·3	26·67	565	411·0	0·3	19·57
585	376·0	1·2	27·15	585	408·5	1·2	20·06
630	376·0	0	27·15	630	406·0	0·5	20·55
655	374·0	0·8	27·53	655	406·0	0	20·55
710	371·0	0·5	28·10	710	403·0	0·5	21·15
775	368·0	0·5	28·69	775	403·0	0	21·15
815	368·0	0	28·69	815	403·0	0	21·15
Blowpipe	367·5	—	28·79	Blowpipe	403·0	0	21·15

V. Hydrate of ZrO_2 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	264·0	—	—
51	230·0	− 9·4	12·89
63	216·0	11·7	18·16
75	211·9	4·2	20·01
87	206·5	3·7	21·79
99	200·5	5·0	24·06
110	197·5	2·7	25·19
123	193·5	3·1	26·72
135	190·0	2·9	28·00
147	187·5	2·1	29·00
159	185·0	2·1	29·88
171	183·5	1·2	30·49
183	182·0	1·2	31·06
195	180·5	1·2	31·63
207	180·0	0·4	31·82
219	179·5	0·4	32·01
231	178·5	0·8	32·29
243	178·0	0·4	32·58
255	177·0	0·8	32·95
267	176·0	0·8	33·33
279	175·0	0·8	33·71
291	174·5	0·4	33·90

VI. Hydrate of SnO_2 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	721·0	—	—
51	685·0	−10·0	5·00
63	649·5	30·0	9·92
75	640·5	7·5	11·17
87	634·5	5·0	11·93
99	628·0	5·4	12·83
110	625·5	2·3	13·18
123	620·5	3·9	13·87
135	616·0	3·7	14·49
147	614·0	1·7	14·77
159	612·0	1·7	15·05
171	610·0	1·7	15·33
183	607·0	2·5	15·74
195	604·5	2·1	16·09
207	603·0	1·2	16·30
219	601·5	1·2	16·51
231	599·5	1·7	16·79
243	597·5	1·7	17·06
255	595·5	1·7	17·34
267	594·0	1·2	17·54
279	592·5	1·2	17·75
291	591·5	0·8	17·96

V. Hydrate of ZrO_2 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
340°	172·5	−0·4	34·66
360	172·0	0·3	34·85
385	170·5	0·6	35·42
415*	160·5	3·3	39·2
440	160·0	0·2	39·39
500	159·5	0·1	39·58
530	159·0	0·2	39·77
565	159·0	0	39·77
585	158·5	0·2	39·96

An accident prevented further heating.

VI. Hydrate of SnO_2 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
340°	587·5	−0·8	18·52
360	586·0	0·8	18·73
385†	580·5	2·2	19·50
415	579·5	0·3	19·63
440	575·5	1·6	20·19
500	574·5	0·2	20·33
530	573·5	0·3	20·47
565	571·5	0·6	20·74
585	567·5	2·0	21·29
630	562·5	1·1	21·98
655‡	562·0	0·2	22·05
710	562·0	0	22·05
775	561·5	0·07	22·12
815	561·5	0	22·12
Blowpipe	559·5	—	22·39

* Changed from grey to pure white.
† Changed from dirty brown to pale yellow.
‡ Took a greenish tinge.

VII. Hydrate of CeO_2 (air-dried for 12 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	644·0	—	—
51	623·5	−5·7	3·18
63	620·0	2·9	3·73
75	617·0	2·5	4·19
87	614·0	2·5	4·66
99	609·0	4·2	5·43
110	606·5	2·3	5·82
123	600·0	5·0	6·83
135	594·5	4·6	7·69
147	584·5	8·2	9·24
159	565·5	15·9	12·19
171	554·0	9·6	13·98
183	552·5	1·2	14·21
195	550·0	2·1	14·60
207	548·0	1·7	14·91
219	546·5	1·2	15·14
231	545·0	1·2	15·37
243	543·5	1·2	15·60
255	542·5	0·8	15·76
267	541·5	0·8	15·92
279	541·0	0·4	16·00
291	540·0	0·8	16·17
340	536·0	0·8	16·77
360	536·0	0	16·77

VIII. Hydrate of PbO_2 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	706·5	—	—
51	696·5	−2·8	1·41
63	695·5	0·8	1·55
75	695·5	0	1·55
87	695·0	0·4	1·63
99	694·5	0·4	1·70
110	693·5	0·9	1·84
123	693·5	0	1·84
135	692·5	0·8	1·98
147	691·5	0·8	2·12
159	690·5	0·8	2·26
171	690·5	0	2·26
183	690·0	0·4	2·33
195	689·5	0·4	2·40
207	689·0	0·4	2·47
219	688·0	0·8	2·61
231	687·0	0·8	2·75
243	686·0	0·8	2·90
255	685·0	0·8	3·04
267	684·5	0·4	3·11
279	684·0	0·4	3·18
291	672·5	9·6	4·86
340	668·0	0·9	5·45
360	668·0	0	5·45

VII. Hydrate of CeO_2 (air-dried for 12 days).				VIII. Hydrate of PbO_2 (air-dried for 10 days.)			
I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.	I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.			mgrms.	mgrms.	
385°*	534·0	−0·8	17·08	385°‡	663·0	−2·0	6·16
415	533·5	0·2	17·16	415	653·0	3·3	7·57
440	533·0	0·2	17·24	440	655·0	+0·8	7·29
500	533·0	0	17·24	500	656·0	0·16	7·15
530	532·5	0·2	17·32	530	656·0	0	7·15
565	531·5	0·3	17·47	565§	643·0	−3·7	8·99
585	531·5	0	17·47	585	641·5	0·7	9·20
630††	518·5	2·9	19·49	630 (fused)	641·5	0	9·20
655	513·5	2·0	20·26	655	641·5	0	9·20
710	494·5	3·4	23·21	710	639·0	0·4	9·55
775	460·5	5·2	28·49	775	639·0	0	9·55
815	433·5 (?)	6·8	32·68 (?)	815	639·0	0	9·55
Blowpipe	437·0	—	32·14				

* Changed from brownish-yellow to bright yellow.
† Turned a pinkish (salmon) colour.
‡ Light specks began to appear in the brown.
§ Became yellow.

IX. Hydrate of Sb_2O_3 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	932·5	—	—
52	932·0	−0·1	0·05
64	931·5	0·4	0·11
76	931·0	0·4	0·16
88	931·0	0	0·16
100	931·0	0	0·16
112	930·5	0·4	0·21
123	930·0	0·4	0·27
135	929·5	0·4	0·32
147	929·5	0	0·32
158	929·5	0	0·32
170	929·5	0	0·32
181	929·5	0	0·32
193	929·5	0	0·32
205	928·5	0·8	0·43
217	927·5	0·8	0·53
229	927·0	0·4	0·59
241	927·0	0	0·59
252	927·0	0	0·59
264	926·5	0·4	0·64
275	926·5	0	0·64
287	926·0	0·4	0·70

X. Hydrate of Bi_2O_3 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	975·0	—	—
52	956·0	−5·1	1·95
64	950·0	5·0	2·56
76	948·0	1·7	2·77
88	946·0	1·7	2·98
100	943·0	2·5	3·28
112	942·0	0·8	3·38
123	939·5	2·3	3·64
135	938·5	0·8	3·75
147	936·5	1·7	3·96
158	935·0	1·4	4·10
170	934·0	0·8	4·21
181	932·0	1·8	4·41
193	929·5	2·1	4·67
205	926·0	2·9	5·02
217	923·5	2·1	5·28
229	921·5	1·7	5·48
241	920·5	0·8	5·59
252	919·5	0·9	5·70
264	918·5	0·8	5·80
275	917·0	1·4	5·95
287	916·5	0·4	6·00

IX. Hydrate of Sb_2O_3 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
298°	926·0	0	0·70
340	925·0	−0·2	0·81
360	925·0	0	0·81
385	938·5	+5·4	gain 0·64
415	942·5	1·3	„ 1·07
440	943·5	0·4	„ 1·18
500	957·0	2·2	„ 2·63
530	958·0	0·3	„ 2·73
565	958·5	0·14	„ 2·78
585	972·0	6·8	„ 4·23
630	976·5	1·0	„ 4·74
655	976·5	0	„ 4·74
710	979·5	0·5	„ 5·04
775	979·0	−0·1	„ 4·98
An accident prevented further heating.			

X. Hydrate of Bi_2O_3 (air-dried for five months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
298°	915·0	−1·4	6·15
340	910·0	1·2	6·67
360	900·5	4·8	7·64
385	890·0	4·2	8·72
415*	868·5	7·2	10·92
440†	866·0	1·0	11·18
500	856·0	1·7	12·21
530	855·0	0·3	12·31
565	853·5	0·4	12·47
585	851·0	1·2	12·73
630	852·0	+0·2	12·63
655	852·0	0	12·63
710 fused	852·5	0·1	12·58
775	852·0	−0·1	12·63
An accident prevented further heating.			

* From light to deep yellow (brown when hot).
† Turned light again.

XI. Hydrate of Al_2O_3 (air-dried for six months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	600·0	—	—
50	550·0	−14·3	8·33
62	494·0	46·7	17·66
74	477·0	14·2	20·50
87	468·5	6·6	21·92
99	462·5	5·0	22·92
111	456·5	5·0	23·92
123	452·5	3·3	24·58
135	449·0	2·9	25·16
147	446·0	2·5	25·66
159	440·5	4·6	26·58
171	436·5	3·3	27·15
183	432·5	3·3	27·91
195	429·0	2·9	28·50
207	425·0	3·3	29·16
219	410·0	12·5	31·66
230	386·0	21·8	35·66
242	379·0	5·8	36·83
254	375·5	2·9	37·42
266	374·5	0·8	37·58
279	373·5	0·8	37·75
291	370·5	2·5	38·25
340	349·5	4·3	41·75
360	342·5	3·5	42·92

XII. Hydrate of In_2O_3 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	134·0	—	—
50	127·5	−1·9	4·85
62	125·5	1·7	6·34
74	124·0	1·2	7·46
87	122·5	1·2	8·59
99	121·5	0·8	9·33
111	120·5	0·8	10·08
123	119·0	1·2	11·19
135	117·5	1·2	12·31
147	116·5	0·8	13·06
159	113·0	2·9	15·67
171	111·5	1·2	16·79
183	110·0	1·2	17·91
195	109·5	0·4	18·29
207	108·5	0·8	19·03
219	107·5	0·8	19·77
230	105·5	1·8	21·27
242	103·5	1·7	22·76
254	101·5	1·7	24·26
266	100·0	1·2	25·37
279	100·0	0	25·37
291	100·0	0	25·37
340	98·5	0·3	26·49
360	98·5	0	26·49

XI. Hydrate of Al_2O_3 (air-dried for six months).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
385°	341·0	−0·6	43·17
415	338·0	1·0	43·67
440	336·0	0·8	44·00
500	333·5	0·4	44·42
530	333·5	0	44·42
565	332·5	0·3	44·59
585	331·0	0·7	44·83
630	329·0	0·4	45·17
655	329·0	0	45·17
710	327·0	0·4	45·50
Blowpipe	323·0	—	46·17

XII. Hydrate of In_2O_3 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
385°	98·5	0	26·49
415	98·0	−0·2	56·86
440	97·5	0·2	27·23
500	97·5	0	27·23
530	97·5	0	27·23
565	97·5	0	27·23
585	97·5	0	27·23
630	97·5	0	27·23
655	97·0	0·2	27·61
710	97·0	0	27·61
775	97·0	0	27·61
815	97·0	0	27 61
Blowpipe	97·0	0	27·61

XIII. Hydrate of Tl_2O_3 (air-dried for 14 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	352·0	—	—
50	347·0	−1·4	1·42
62	346·5	0·4	1·56
74	346·0	0·4	1·70
87	345·5	0·4	1·84
99	345·0	0·4	1·99
111	344·5	0·4	2·13
123	344·0	0·4	2·27
135	343·0	0·8	2·56
147	342·5	0·4	2·70
159	342·5	0	2·70
171	342·5	0	2·70
183	342·5	0	2·70
195	342·0	0·4	2·84
207	341·5	0·4	2·98
219	341·5	0	2·98
230	341·0	0·5	3·13
242	341·0	0	3·13
254	341·0	0	3·13
266	341·0	0	3·13
279	341·0	0	3·13
291	341·0	0	3·13

XIV. Hydrate of Fe_2O_3 (air-dried for 18 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	862·5	—	—
50	777·5	24·3	9·86
62	677·5	83·3	21·45
74	645·5	26·7	25·16
86	623·5	18·3	27·71
98	611·5	10·0	29·10
110	598·0	11·2	30·67
122	590·5	6·2	31·54
134	584·0	5·4	32·29
146	578·5	4·6	32·92
158	573·5	4·0	33·51
170	568·0	4·6	34·14
182	564·0	3·3	34·61
194	562·5	1·2	34·78
206	560·0	2·1	35·07
218	557·5	2·1	35·36
230	555·5	1·7	35·59
244	553·5	1·5	35·82
257	553·0	0·4	35·88
269	552·5	0·4	35·94
281	552·0	0·4	36·00
293	550·5	1·2	36·17

XIII. Hydrate of Tl_2O_3 (air-dried for 14 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
340°	341·0	0	3·13
360	341·0	0	3·13
385	340·0	−0·4	3·42
415	338·0	0·7	3·98
440	337·0	0·4	4·27
500	337·0	0	4·27
530	337·0	0	4·27
565	337·0	0	4·27
585*	335·5	0·8	4·69
630 fused†	301·5	7·6	14·35
655	290·0	4·6	17·61
710	268·5	3·9	23·72
775	244·0	3·8	30·68
815	239·5	1·1	31·96
Blowpipe	239·5	0	31·96

XIV. Hydrate of Fe_2O_3 (air-dried for 18 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
	mgrms.	mgrms.	
340°	550·0	0·1	36·23
360	548·5	0·8	36·40
385	540·5	3·2	37·32
415	540·5	0	37·32
440	536·5	1·6	37·79
500	534·5	0·3	38·03
530	534·5	0	38·03
565	534·5	0	38·03
585	534·5	0	38·03
630	534·5	0	38·03
655	534·5	0	38·03
710	534·5	0	38·03
Blowpipe	534·0	—	38·09

* Lost its gloss and became dull-black.
† To a dirty green liquid.

XV. Hydrate of Co_2O_3 (air-dried for 15 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	397·5	—	—
50	397·5	0	0
62	397·5	0	0
74	397·5	0	0
80	396·5	0·8	0·25
98	395·5	0·8	0·50
110	393·5	1·7	1·01
122	391·0	2·1	1·63
134	389·5	1·2	2·01
146	388·0	1·2	2·38
158	387·0	0·8	2·64
170	386·0	0·8	2·89
182	385·0	0·8	3·14
194	384·0	0·8	3·40
206	382·0	1·7	3·90
218	378·0	3·3	4·91
230	370·0	6·7	6·92
244	360·0	7·1	9·43
257	346·0	10·7	12·95
269	341·0	4·2	14·22
281	340·0	0·8	14·47
293	340·0	0	14·47

XV. Hydrate of Co_2O_3 (air-dried for 15 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
340	339·5	0·1	14·59
360	339·0	0·2	14·71
385	336·5	1·0	15·34
415	336·5	0	15·34
500	336·5	0	15·34
530	336·5	0	15·34
565	336·5	0	15·34
585	336·5	0	15·34
630	336·5	0	15·34
655	336·0	0·2	15·47
710	336·0	0	15·47
775	336·0	0	15·47
815	336·0	0	15·47
Blowpipe	336·0	0	15·47

XVI. Hydrate of Ni_2O_3 (air-dried for 10 days).

I. Temperature.	II. Weight.	III. Difference from previous weighing for an increase of 10°.	IV. Loss per cent.
°	mgrms.	mgrms.	
15	864·5	—	—
50	792·0	20·7	8·38
62	715·0	64·2	17·29
74	700·5	12·1	18·97
86	689·0	9·6	20·30
98	680·5	7·1	21·28
110	669·5	9·2	22·55
122	659·0	8·7	23·77
134	648·5	8·7	24·99
146	637·5	9·2	26·26
158	623·5	11·7	27·88
170	601·0	18·7	30·32
182	587·5	11·2	32·04
194	579·0	7·1	33·02
206	573·0	5·0	33·72
218	570·0	2·5	34·07
230	567·0	2·5	34·41
244	564·5	1·8	34·71
Stopped	by an accident	at this point.	

As regards the several curves the following remarks will explain the results indicated:—

I. *Hydrate of* Ag_2O.—The precipitate obtained on adding caustic soda to a solution of silver nitrate absorbed a very small quantity of carbonic anhydride on drying. The product after drying in the air for six months appeared to be the normal hydroxide AgOH. On heating, this was comparatively stable up to about 100°, but on further heating it lost water and a small quantity of oxygen, and was converted gradually into Ag_2O (admixed with a small quantity of metallic silver). At a higher temperature, the whole of the oxygen was given off, leaving a residue of pure silver.

The various phenomena, therefore, were:—

(1.) AgOH comparatively stable up to about*... 100°

(2.) Rapid loss of water and small quantity of oxygen*..... 100—180°

* *Watts' Dictionary*, 5, 302, states that precipitated silver oxide becomes anhydrous on drying at 60—70°; and that it gives off a certain quantity of oxygen at 100°, but whether Ag_4O or Ag is thus formed is not known (comp. Bailey, Trans., 1887, 416; and v. der Pfordten, *Ber.*, 20, 1468).

(3.) Ag_2O (containing a small quantity of Ag) comparatively stable	180—270°
(4.) Rapid decomposition of Ag_2O with reduction to metallic silver*.....	270—300°
(5.) Reduction complete at about	300—340°

II. *Hydrate of* HgO.—The precipitate obtained on adding caustic soda to a solution of mercuric chloride, after drying in the air for five months, had the composition $Hg(OH)_2$. On heating this remained tolerably stable up to about 100°, at which temperature (after heating in all about 10 hours) it had lost only about one-half per cent. of its weight, whereas complete dehydration to HgO would require a loss of nearly 8 per cent. Above 100°, it lost water more and more rapidly, and became completely dehydrated to HgO at about 175°. Above this temperature, incipient decomposition into mercury and oxygen commenced and continually increased up to about 360°, when it became much more rapid, and developed into full decomposition at from 415° to 440°. The changes in colour which the substance exhibits *when cold* after heating above 360° are noteworthy. After heating from 360° to 385°, the colour had changed from brown to yellow specked with white. These specks disappeared on heating from 415° to 440°, and the whole became bright orange. This last change probably indicated the conversion of the yellow oxide into the more stable allotropic ordinary red oxide of mercury.

We have therefore :—

(1.) $Hg(OH)_2$ almost stable up to about†.....	100°
(2.) Rapid dehydration	110—175°
(3.) Complete dehydration to HgO about.....	175°
(4.) Incipient decomposition into Hg and O‡....	175—360°
(5.) Full decomposition sets in, whilst the still undecomposed HgO changes from the yellow to the red modification,‡ about	415—440

III. *Hydrate of* SiO_2.—The precipitated silica obtained on adding hydrochloric acid to a solution of sodium silicate, after air-drying for

* Pure Ag_2O begins to give off oxygen at 250° (*Watts' Dictionary*, **1**, 792).

† According to *Watts' Dictionary*, **3**, 908, yellow mercuric oxide is anhydrous, whereas Schaffner (*Annalen*, **51**, 181) states that the yellow precipitate formed by the addition of caustic potash to mercuric salts is the hydrate $HgO,3H_2O$.

‡ These results, obtained by heating in a covered but *not air-tight* crucible, are in accord with those of Meyers (*Ber.*, **6**, 11), who determined the course of the decomposition by the tension of the gas evolved. Debray (*Compt. rend.*, **77**, 123), however, has shown that if the mercury and oxygen be heated in a *sealed tube* maintained *throughout at a uniform temperature*, the oxygen is almost completely absorbed by the mercury even at 440°.

five months, retained a quantity of water corresponding very nearly to the formula $3SiO_2,4H_2O$. On heating, this lost water at an almost uniform rate up to 63°, passing through the compositions indicated by SiO_2,H_2O and $2SiO_2,H_2O$, without showing any indication of the formation of definite hydrates of this or other composition. At about 63°, the curve turns upward rather sharply, and thence assumes almost a straight line until it reaches the position for anhydrous silica at a temperature somewhat above 815° (say 850°).*

These results show that precipitated silica when heated at successively increasing temperatures forms no hydrates which are stable through a range of temperature of at most 13°. The phenomena are in fact such as to indicate that probably numerous successive hydrates are formed as the temperature increases, but that all these are so very unstable that a small further rise in temperature causes an additional loss of water. The rapid rise of the curve above 63° would seem to show either that the hydrates formed below were much less stable than those formed above that temperature, or more probably that the latter were much more complicated in composition.

It was at one time supposed that hydrates of a definite and constant composition could be obtained by drying gelatinous silica under various conditions, and the following have been stated to exist by different observers :—

Dialysed silicic acid.....	$SiO_2,2H_2O$.
Dried at ordinary temperature	SiO_2,H_2O.
„ 20—25°.....	$2SiO_2,H_2O$.
„ 60°	$3SiO_2,H_2O$.
„ 80—100°	$4SiO_2,H_2O$.
„ 250—270°.....	$8SiO_2,H_2O$.

More recent investigations, however, have shown that the quantity of water contained in the artificial, as well as in the natural amorphous silica, varies within very considerable limits, whilst the water can be driven off at such low temperatures that it has been suggested that this water is, to some extent at least, mechanically admixed, and that at any rate these hydrates must be considered to be very loose compounds of silica and water (Roscoe and Schorlemmer's *Treatise on Chemistry*, **1**, 572). This is entirely confirmed by our results.

IV. *Hydrate of* TiO_2.—This curve is very similar to that for silica, and similar remarks, therefore, apply in this case. The chief differ-

* By the term "stable hydrate" as used in this paper, is meant a hydrate which undergoes no loss of weight on further heating through an appreciable range of temperature above that at which it had been formed by the dehydration of a higher hydrate, whereas a hydrate which is unstable is one which loses more water on a slight rise of temperature above that at which it had been formed.

ence is that the steep upward turn of the curve is not nearly so abrupt as for the hydrates of silica. Titanic acid becomes completely dehydrated at about 710°. A very large number of hydrates of TiO_2 are said to have been obtained, for a list of which see *Watts' Dictionary*, **6**, 1098. As in the case of the silicic hydrates, it is very doubtful whether these are of definite or constant composition (compare Rose, *Annalen*, **53**, 267; *Gmelin's Handbook*, **3**, 475; Roscoe and Schorlemmer's *Treatise*, **2**, ii, 259). The regular and unbroken form of the curve obtained by us is certainly against the existence of definite hydrates of any evident degree of stability.

V. *Hydrate of* ZrO_2.—With one or two marked exceptions, this curve indicates that phenomena occur on heating similar to those in the case of silicic and titanic hydrates. The upward turn of the curve takes place even more gradually than with titanic acid. The two special characteristics of this curve, however, are:—(1) For temperatures below 385° it shows that though the percentage loss is greater at any given temperature, yet a much greater quantity of water is retained per molecule of ZrO_2 than in the case of either SiO_2 or TiO_2. Thus, whereas silica is dehydrated to $2SiO_2,H_2O$ at about 60°, and titania to $2TiO_2,H_2O$ at about 70°, zirconia is dehydrated to $2ZrO_2,H_2O$ only at 385°. (2) The most noteworthy difference, however, is the sudden break in the continuity of the curve between 385° and 415°, the sudden increase in the loss per degree of rise in temperature being much greater than it had been for the previous 280°. Unfortunately no observation was made between 385° and 415°, but somewhere between these temperatures a very sudden increase in the elimination of water took place; for, whereas the hydrate at 385° had the composition $2ZrO_2,H_2O$, it had at 415° the composition $24ZrO_2,H_2O$, and soon after became completely anhydrous.

Curiously enough, this phenomenon was accompanied by a change in colour from grey to pure white, whilst other observers state that this change in colour occurs at the same time as a vivid incandescence, and a considerable modification in the chemical properties of the zirconia. Owing to the conditions of the experiment, we could not tell whether this incandescence took place or not. The peculiar incandescence referred to was first noticed by Sir Humphry Davy, whilst Chevreul observed that it was preceded by blackening; the latter was ascribed by Hermann to the presence of impurities (compare *Gmelin's Handbook*, **3**, 342). Gmelin states (*loc. cit.*) that zirconia becomes anhydrous considerably below red heat, and that the above incandescence only occurs after all the water has been driven off. This must be an error, as we found that at or very near the temperature at which incandescence takes place the composition was represented by $2ZrO_2,H_2O$, and that even after the incandescence

a loss of at least 0·76 per cent. occurred on further heating to 585°. The actual loss on complete dehydration may possibly have been even slightly greater, for an accident unfortunately prevented heating to a higher temperature. These results seem to show that the incandescence which occurs at about 400° is not due as hitherto supposed to the conversion of one form of anhydrous zirconia into a denser and more stable modification, but to the sudden elimination of water, accompanied probably by a considerable condensation of the zirconia from the comparatively small molecule $n(2ZrO_2,H_2O)$ to the large molecule $n(24ZrO_2,H_2O)$.

The form of the curve appears to indicate that no definite stable hydrate is formed by heating precipitated zirconia, and this is confirmed by the discordant results obtained by other observers, thus :— According to Berzelius, the dry hydrate has the composition, ZrO_2,H_2O = 12·9 per cent. H_2O, whereas Davy stated that it contained 20 per cent., and Klaproth gave as much as 33 per cent. Hermann found that the hydrate dried at 17° was represented by $ZrO_2,2H_2O$ = 23 per cent.

VI. *Hydrate of* SnO_2.—This curve is very similar to those for silica and titania and, like them, shows that no definite stable hydrates were formed. The oxide became anhydrous at 630—655°. A little above 360°, it had the composition indicated by $3SnO_2,H_2O$, and was of a dirty-brown colour. On a further small rise in temperature, it suddenly changed from brown to pale yellow, and simultaneously lost weight at a rate nearly three times as great as during the previous 100°, after which the rate of loss during the next 30° or 40° was reduced to less than one-seventh of that which occurred during the change of colour. After changing colour, it had the composition $7SnO_2,2H_2O$.

The following stannic hydrates are said to have been obtained by different observers :—

(*a.*) *Of ordinary Stannic Acid*, SnO_2,H_2O. (By action of Acids on Soluble Stannates.)

Dried in stream of dry air (Fremy)	$3SnO_2,7H_2O$.
Dried at ordinary temperature in air (Weber)	$SnO_2,2H_2O$.
Dried in a vacuum (Fremy)	SnO_2,H_2O.
Dried at 140° (Fremy)	$3SnO_2,2H_2O$.

(*b.*) *Of Metastannic Acid*, $Sn_5O_{10},5H_2O$. (By oxidation of Tin with Nitric Acid.)

Dried at ordinary temperature (Fremy)....	$5SnO_2,10H_2O$,
,, ,, (?) (Berzelius)	SnO_2,H_2O.
,, ,, (Thomson)..	SnO_2,H_2O.
Dried over sulphuric acid (Weber).....	SnO_2,H_2O.
Dried in a vacuum or at 100° (Fremy)	$5SnO_2,5H_2O$.
Dried at 130° (Fremy)	$5SnO_2,4H_2O$.
Dried at 160° ,, ...	$5SnO_2,3H_2O$.
Dried at 55° (Thomson).....	$2SnO_2,H_2O$.

(*c.*) *Intermediate Acids* (*Musculus*), $Sn_2O_4,2H_2O$ *and* $Sn_3O_6,3H_2O$.

VII. *Hydrate of* CeO_2.—This curve is a characteristic one, and is distinguished from those of the other metals of the silicon-group, which it otherwise resembles to temperatures of about 600°, by the fact that after rising almost perpendicularly from 200° to 600°, it begins at the latter temperature to curve towards the horizontal, and this continues even up to 815°. The composition at 600°, just before this change occurs, is represented by $CeO_2,2H_2O$. This would seem to be a definite hydrate, for the composition had previously remained nearly constant, the loss of water for 12 hours between 385° and 600° not having amounted to more than 0·39 per cent., or for eight hours' heating between 440° and 600° to 0·23 per cent. Further, the rate of loss which commences at 600° is 20 times as great as the average rate during the previous 220°, and, moreover, at 600° the colour suddenly changes from a light yellow (presumably the colour of the hydrate $CeO_2,2H_2O$) to salmon colour, the latter prevailing until complete dehydration. Finally, at the temperature at which the composition became practically constant (385°), and therefore presumably that at which the hydrate $Ce_2O,2H_2O$ was formed, there was a change of colour from brownish-yellow to bright-yellow. We may therefore conclude that ceric oxide forms a definite hydrate, $CeO_2,2H_2O$, or normal ortho-ceric hydrate, H_4CeO_4 or $Ce(OH)_4$, which is very nearly stable even up to 600°, at which temperature rapid dehydration begins. We have, as regards colour, the following:—

Hydrates, $CeO_2,(2 + a)H_2O$.....	brownish-yellow.
Hydrate, $CeO_2,2H_2O$	bright-yellow.
Hydrates, $CeO_2,(2 - b)H_2O$.....	salmon colour.
Anhydrous oxide, CeO_2	ditto.

Pure cerium dioxide is said to be a white or pale straw-coloured powder, but that after an hour's ignition it acquires a reddish tinge

(Mosander). Watts states that it is fawn- or salmon-coloured. The hydrate precipitated from ceric salts by alkalis is pale or sulphur-yellow according to Berzelius and Mosander, but they do not state what its composition is. A sulphur-yellow hydrate, of the formula $2CeO_2,3H_2O$, is formed on heating the acid sulphate with caustic potash, or by the action of chlorine on the hydroxide of the sesqui-oxide suspended in water (Roscoe and Schorlemmer, *Treatise*, **2**, i, 428).

VIII. *Hydrate of* PbO_2.—This curve has a form quite different from those for SiO_2, SnO_2, &c., owing to the decomposition which the oxide itself undergoes on heating, being ultimately converted into PbO and O. Precipitated lead dioxide, after drying in the air for 10 days, had very nearly the composition $3PbO_2,H_2O$. On heating, it gradually lost water and became dehydrated to PbO_2 at about 230°, on further heating, its weight remained nearly constant up to 280°, at which temperature it suddenly lost oxygen and was converted into Pb_2O_3. This was stable up to about 365°, when a further loss of oxygen occurred, with the formation of Pb_3O_4; the latter was stable up to 530—565°, when it lost more oxygen, became yellow, and formed PbO; this last change being complete at 585°. The PbO thus formed subsequently fused between 585° and 630°.

We have therefore—

Hydrate dried in air = $3PbO_2,H_2O$.	
Complete dehydration to PbO_2 at about..	230°
PbO_2 stable up to about	280
Loss of oxygen with formation of Pb_2O_3..	280—290°
Pb_2O_3 stable between about	290—360
Loss of oxygen with formation of Pb_3O_4..	360—415
Pb_3O_4 stable between about	415—530
Loss of oxygen with formation of PbO...	530—580
PbO stable from.....	580 to above 815°
PbO fused somewhere between	585—630°

Becquerel (*Ann. Chim. Phys.* [3], **8**, 405) states that the hydrate, PbO_2,H_2O, is deposited at the positive pole during the electrolysis of lead salts. This is the only previous notice of a hydrate of PbO_2. The difficulties which occur in the manufacture of red lead from massicot (PbO) are doubtless due to not employing the most suitable temperature. Mercier (*Annalen*, **160**, 252) says that the principal point to be attended to, next to the access of sufficient air, is *constancy of the right temperature;* for the temperature at which massicot takes up oxygen and that at which red lead loses it lie very near to each other. He states that the most favourable temperature approaches that of a dull-red heat, without, however, reaching it. The results

we have given above may possibly be of service in this important manufacture.

IX. *Precipitated* Sb_2O_3.—Precipitated antimony trioxide, after drying in the air for five months, was found to be anhydrous. On heating, it underwent but a slight loss in weight, and appeared to be very nearly stable up to 360°, at which temperature it took up oxygen, forming an oxide approximating to $Sb_{20}O_{32}$; this remained comparatively constant between 415° and 440°, gaining only 0·11 per cent. in weight. Above 440°, it again took up oxygen with the formation apparently of Sb_4O_7. This remained comparatively constant up to about 565°; above 565° it again took up oxygen with the formation of Sb_2O_4, which then remained stable up to 775°, which was the highest temperature reached.

We have therefore—

$Sb_{20}O_{30} = 5Sb_4O_6 = 10Sb_2O_3$ stable up to ..	360°
Rapid absorption of oxygen	360—400°
$Sb_{20}O_{32}$ comparatively stable	415—440
Rapid absorption of oxygen somewhere between.....	440—500
$Sb_{20}O_{35} = 5Sb_4O_7$ comparatively stable.....	500—565
Rapid absorption of oxygen	565—585
$Sb_{20}O_{40} = 5Sb_4O_8 = 10Sb_2O_4$ stable	590 to above 775°

Antimony trioxide is usually said to be anhydrous; Regnault, however (*Cours de Chimie*, **3**, 239), describes the hydrate Sb_2O_3,H_2O, and Schaffner (*Annalen*, **51**, 168) the hydrate $Sb_2O_3,2H_2O$; but neither of these was prepared by direct methods.

X. *Hydrate of* Bi_2O_3.—The precipitated hydrate, after drying in the air for five months, had nearly the composition $Bi_2O_3,3H_2O$;* this hydrate was not stable, but on heating lost water gradually up to 340°, and then much more rapidly up to 415°, at which temperature it contained less water than corresponds to the formula Bi_2O_3,H_2O. It became completely dehydrated at about 600°, and afterwards fused somewhere between 655° and 710°. There did not appear to be any decisive indication of a definite hydrate of any evident degree of stability. Muir states (*Chem. Soc. Jour.*, 1877, i, 648—649) that the following hydrates of bismuth trioxide are known:—$Bi_2O_3,3H_2O$; $Bi_2O_3,2H_2O$; Bi_2O_3,H_2O.

An inspection of Curve No. X, however, shows that none of these are stable, or only through a very small range of temperature, and

* It also contained some carbonic acid, so that the results obtained in this case cannot be considered as conclusive.

that on heating, the highest hydrate passes *gradually* into the lowest, and finally into the anhydrous oxide.

XI. *Hydrate of* Al_2O_3.—The precipitated hydrate of alumina, after drying in the air for six months, had the composition $Al_2O_3,5H_2O$. It attained the composition $Al_2O_3,3H_2O$ on heating at 65°, after which the rate of loss diminished considerably up to about 150°, when it again increased up to 160°, and again diminished up to about 200°. Between 160° and 200°, the composition approximated to $Al_2O_3,2H_2O$. From 200° to 250°, the rate of loss was again very rapid, but became very much less between 250° and 290°, when the composition was approximately Al_2O_3,H_2O. Above 290°, the rate of loss rapidly increased again up to 360°, beyond which it slackened, and water was gradually but slowly expelled until complete dehydration was reached at a temperature of about 850°. At no point did the composition remain constant, an increase of 10° always caused a further loss of water, except at temperatures above 500°, when the alumina was very nearly dehydrated. A certain *comparative*—but only comparative—stability, however, was attained at or about the three following temperatures, viz.:—

$Al_2O_3,3H_2O$ *comparatively* stable.....	65—150°
$Al_2O_3,2H_2O$ „ „	160—200
Al_2O_3,H_2O „ „	250—290

The following hydrates have been previously noticed:—

Precipitated at a boiling heat and dried at ordinary temperature (Ramsay).....	$Al_2O_3,5H_2O$.
Hydrargillite and gibbsite; also the artificial hydrate obtained by precipitation and dried (in air?) (Torrey, Berzelius, Bonnsdorff)	$Al_2O_3,3H_2O$.
By heating aluminium acetate at 100° for some days and drying the resulting precipitate at 100° (Crum)	$Al_2O_3,2H_2O$.
By prolonged ebullition of $Al_2O_3,3H_2O$ suspended in water (St. Gilles)	$Al_2O_3,2H_2O$.
Native hydrate from Beaux (Berthier)...	$Al_2O_3,2H_2O$ (?).
Diaspore	Al_2O_3,H_2O.
Precipitated hydrate dried at 300° (Ramsay).....	Al_2O_3,H_2O.
Al_2O_3,H_2O does not part with its water below 360° (Dufrénoy).	

Our results agree very closely with the above and with those of

Ramsay on the dehydration of alumina (*Chem. Soc. Jour.*, 1877, ii, 395). Ramsay's and our own results show either that there are no definite stable hydrates of alumina, or what is more probable, that a very large number of hydrates exist, but so unstable that the smallest rise in temperature is sufficient to convert a higher into a lower hydrate.

XII. *Hydrate of* In_2O_3.—The air-dried hydrate had very nearly the composition $In_2O_3,6H_2O$. On heating, it lost water gradually, and at a nearly uniform rate up to 150°, when it had the composition $In_2O_3,3H_2O$. The rate of loss then rapidly increased up to 160°, beyond which it proceeded almost uniformly at the previous rate, and the substance passed successively through the compositions $In_2O_3,2H_2O$, $2InO_3,3H_2O$, and In_2O_3,H_2O, without giving any evidence of the formation of a stable hydrate. Soon after passing through In_2O_3,H_2O, and at about 280°, the rate of loss suddenly diminished, the curve taking a sharp curve upward, and becoming nearly perpendicular. Complete dehydration, however, was finally attained only at 655°, the last traces of water being lost very slowly.

The two following hydrates are said to have been obtained (*Watts' Dict.*, **6**, 732):—

Hydrate precipitated at boiling heat and air-dried	$2In_2O_3,7H_2O$.
Dried at 100°	$In_2O_3,3H_2O$.

But generally speaking the same remarks apply here as in the case of alumina, in so far as there is no indication of the formation of any definite stable hydrates.

XIII. *Hydrate of* Tl_2O_3.—Precipitated and air-dried thallic hydrate had almost exactly the composition Tl_2O_3,H_2O. This, however, was not stable, but on heating gradually lost water until complete dehydration was attained at about 230°. The weight then remained perfectly constant up to 360°, between which and 440° a further very slight diminution occurred, due apparently to loss of oxygen. Above 440°, and up to between 565° and 585°, the weight again remained perfectly constant, and corresponded exactly to $3Tl_2O_3,Tl_2O$. Somewhere between 565° and 585° the substance lost its gloss, and became dull black. It then rapidly lost weight, owing partly to loss of oxygen, and partly to volatilisation of the Tl_2O formed. It fused at 630° to a dirty-green liquid. It continued rapidly to lose weight up to 815°, but above this temperature the weight again remained constant, and no further loss occurred on heating over the blowpipe; the total loss then amounted to 31·96 per cent. The final product probably consisted of undecomposed Tl_2O_3. It could not be Tl_2O, as the latter is readily volatile at the temperature employed. The most

probable explanation seems to be that at 585° Tl_2O_3 loses oxygen with partial conversion into Tl_2O, but above 815° any Tl_2O so formed again takes up oxygen, re-forming non-volatile Tl_2O_3. We have therefore—

Air-dried at 15° = Tl_2O_3,H_2O, but unstable on heating.	
Complete dehydration with formation of Tl_2O_3 about	230°
Tl_2O_3 perfectly stable	230—360°
Reduction to $3Tl_2O_3,Tl_2O$	360—440
$3Tl_2O_3,Tl_2O$ perfectly stable	440—565
Rapid loss of oxygen and volatilisation of Tl_2O formed, the rate of loss gradually diminishing after fusion at 630°	585—815
Remaining Tl_2O_3 constant	from 815° upwards.

The following observations have been noted by others :—

Precipitated thallic hydrate dried at 100° (Werther)	Tl_2O_3,H_2O.
Ditto dried over sulphuric acid (Birnbaum)	Tl_2O_3,H_2O.
Ditto dried at 100° (Birnbaum)	Tl_2O_3.
Ditto dried at 260° (Crookes)	Tl_2O_3.

Pure anhydrous Tl_2O_3 melts at 759° (Carnelley); Tl_2O_3 gives off oxygen at a red heat with reduction to Tl_2O (*Watts' Dict.*, 5, 753); Tl_2O melts at about 300°, and at higher temperatures volatilises and partially oxidises at the same time to Tl_2O_3 (*ibid.*, 752).

XIV. *Hydrate of* Fe_2O_3.—Precipitated ferric hydrate, after drying at about 15° for 18 days, contained more water than corresponded to $Fe_2O_3,5H_2O$. On heating, it attained the composition $Fe_2O_3,3H_2O$ at about 55°, but with a further rise in temperature water was *gradually* given off until the oxide was completely dehydrated at 500°; beyond this there was no more alteration in weight. The curve shows that at no point was there any indication of the formation of a definite hydrate, stable through a further rise in temperature, except that at about 385° a hydrate was formed represented exactly by $10Fe_2O_3,H_2O$; this remained perfectly constant in weight on heating for two hours from 385° to 415°, and was possibly stable through a much larger range of temperature.

Ramsay (*Chem. Soc. J.*, 1877, ii, 395) has also investigated the dehydration of ferric hydrate, and he also concludes that no definite stable hydrates are formed, except perhaps Fe_2O_3,H_2O; our results, however, give no indication of the formation of the latter.

The following minerals are well-known natural crystallised hydrates :—

Limonite	$Fe_2O_3,3H_2O$.
„	$Fe_2O_3,2H_2O$.
Göthite	Fe_2O_3,H_2O.
Limonite	$2Fe_2O_3,3H_2O$.
Turgite	$2Fe_2O_3,H_2O$.
„	$3Fe_2O_3,5H_2O$.

The following have been prepared artificially:—

Precipitated when cold (Wittstein)	$Fe_2O_3,3H_2O$.
„ „ (Gmelin and Lefort)	$Fe_2O_3,2H_2O$.
„ „ hot (Lefort, Schaffner)	$Fe_2O_3,2H_2O$.
„ when cold and dried at 100° (Muck)	$Fe_2O_3,2H_2O$.
„ and dried in a vacuum	$2Fe_2O_3,3H_2O$.
By freezing ferric hydrate suspended in water	$2Fe_2O_3,3H_2O$.
Precipitated when cold (Peau St. Gilles)	$2Fe_2O_3,3H_2O$.
Precipitated and dried at 100 (Muck)	Fe_2O_3,H_2O.
Prolonged ebullition of hydrate in water (Peau St. Gilles)	Fe_2O_3,H_2O.
Ferric hydrate dried at 100°	$2Fe_2O_3,H_2O$.
Totally dehydrated by prolonged ebullition in water to	Fe_2O_3.
Precipitated and dried at temperatures between 15° and 100° gives hydrates intermediate between $Fe_2O_3,2H_2O$ and Fe_2O_3,H_2O (Muck).	

XV. *Hydrate of* Co_2O_3.—Air-dried precipitated cobaltic oxide had almost exactly the composition $5Co_2O_3,8H_2O$. At this it remained perfectly constant on heating for six hours at temperatures ranging up to 74°. When heated beyond this, it gradually lost water, and at 100° had exactly the composition $2Co_2O_3,3H_2O$; the latter, however, was not stable, for on further heating it lost more water at a rate which gradually increased up to 260°, when the rate of loss rapidly diminished, the curve turning sharply upwards, and becoming very nearly perpendicular. The product had now exactly the composition $10Co_2O_3,H_2O$ (or Co_2O_3, see below), and at this it remained almost constant (losing but 1 mgrm.) between 280° and 360°. At the latter temperature, it underwent a further slight loss, and became completely dehydrated at 385°, or possibly lost a small quantity of oxygen, giving a product consisting of Co_2O_3 admixed with a little Co_3O_4 (see below).

We have therefore—

Air-dried cobaltic hydrate, $5Co_2O_3,8H_2O$, stable up to	75°
Gradual loss of water without formation of stable hydrate	75—270°
$10Co_2O_3,H_2O$ (or else pure Co_2O_3) stable	280—360
Complete dehydration or slight loss of oxygen with formation of a small quantity of Co_3O_4..	385°

Winkelblech states that precipitated hydrate of cobalt after drying over sulphuric acid has the composition $Co_2O_3,3H_2O$, whereas Hess found that under the same conditions it had the composition $Co_2O_3,2H_2O$. When cautiously heated to 600° or 700°, it yields the anhydrous oxide (*Watts' Dict.*, **1**, 1049). Exposed to a low red heat, it loses oxygen with formation of Co_3O_4 (Hess, Braun; comp. also Russell, *Chem. Soc. J.*, 1863, **16**, 51).

XVI. *Hydrate of* Ni_2O_3.—The completion of the dehydration in this case was prevented by an accident, so that no definite conclusions are possible, except that so far as the curve runs there was no indication of the formation of any definite stable hydrate.

A general consideration of all the curves shows—

(1.) That in no instance [except in the case of $Ag(OH)$, $Hg(OH)_2$, $CeO_2,2H_2O$, and perhaps $5Co_2O_3,8H_2O$] is there any certain indication of the formation of definite hydrates which are stable* through any but possibly a very small range of temperature. From this we must conclude either that there are no definite hydrates formed on heating the precipitated hydrates at gradually increasing temperatures; or that a very large number of such hydrates are formed under these conditions, but that they are so unstable that a very small further rise in temperature is sufficient to convert a higher into a lower hydrate.

If the first alternative be correct, then the so-called hydrates would be mechanical mixtures of the oxide with water, but this is a supposition which is very improbable, for it would be difficult to suppose that mechanically admixed water could be retained at the high temperatures frequently required to produce complete dehydration, in some cases a full red heat.

The second supposition that there are a large number of definite but unstable hydrates formed is far more probable. That definite hydrates of Fe_2O_3,Al_2O_3, &c., exist is proved by their natural occurrence in the form of several well-crystallised minerals, and by the artificial production of many crystallised hydrates. The forms of the dehydration curves would also, one would think, be far more regular did the dehydration consist in the expulsion of merely mechanically

* For definition of "stable hydrate" see p. 81.

admixed water, whereas their greater or less irregularity in most cases seems to indicate the formation of hydrates at certain temperatures which are relatively more stable than hydrates formed at other temperatures. The unstable character of the hydrates is further shown by the frequently discordant results obtained by different observers, and by the apparently slight circumstances which seem in many cases to influence the quantity of water retained by an oxide. The summary of previous work on this subject given above at the end of the discussion of each curve will serve to illustrate this.

In view then of the following facts—

1. That certain well-defined hydrates are known, which are stable through a considerable range of temperature, though the number of these is smaller than is usually supposed;

2. That many well-defined and well-crystallised hydrates are found as minerals, and may also be obtained artificially;

3. That the artificial hydrates produced by heat and of the same composition as these minerals, on further heating lose water more or less gradually at or only very slightly above the temperature at which they were formed;

4. That the temperatures required for complete dehydration are often high;

5. That the dehydration curves frequently seem to indicate the formation of hydrates, which though unstable themselves, except through a very small increase of temperature, are relatively much more stable than other hydrates of the same oxide:—

We conclude that when a precipitated oxide is heated, it gradually loses water with the successive formation of a large number of definite hydrates, each of which is further decomposed on a small rise in temperature with the formation of a hydrate containing a smaller proportion of water. As the elimination of water proceeds, the molecule becomes larger and more and more complex, until ultimately, when the last molecule of water is given off, a highly complex molecule of the anhydrous oxide is left, its formula being some multiple $n(RO_x)$ of the generally received simple formula RO_x.

The polymeric character of the oxides we have examined seems to accord fully with our results, and this taken in connection with the facts and arguments advanced by Henry (*loc. cit.*) seems to prove, or at least to give a very high degree of probability to, the truth of his theory that the known metallic oxides are polymerides $n(RO_x)$ of the unknown simple oxides RO_x. If this be so, then our results also show that in most cases, especially those of SiO_2, TiO_2, Al_2O_3, &c., the coefficient n of polymerisation must be very large: thus, for the oxides of silicon, titanium, and tin it would be at least 10, and probably much higher, so that the molecules of these oxides would be

at least $R_{10}O_{20}$; whilst oxide of zirconium would be at least $Zr_{24}O_{48}$, ferric oxide at least $Fe_{20}O_{30}$. In the case of antimonious oxide the results seem to indicate $Sb_{20}O_{30}$ as the smallest value of its molecule.

The most infusible oxides, such as silica, titania, stannic oxide, alumina, &c., are those which the curves would indicate as having the highest coefficient of polymerisation, and this is what one would expect if the theory of polymerisation be true.

Dehydration and the Periodic Law.

Having now considered the question of the polymerisation of the oxides, we next turn to the second problem which we had in view in commencing this research, viz.:—The relation of the phenomena of the dehydration of the oxides to the Periodic Law.

In dealing with this question, the difference between affinity in *intension* and in *extension* must be well borne in mind. The affinity of sodium for chlorine in sodium chloride is greater in *intension* than that of tin for chlorine in stannic chloride, in so far as the force of combination between one atom of sodium and one atom of chlorine is greater than between the atom of tin and any one of the atoms of chlorine. On the other hand, the affinity of tin for chlorine is greater in *extension* than that of sodium for chlorine, in so far as one atom of tin is capable of combining with four atoms of chlorine, whereas one atom of sodium can combine with one atom of chlorine only.

In like manner, the affinity of two oxides for water may differ from one another. An oxide may combine with but a small quantity of water, but it may retain that with great force, whereas another oxide may combine with a greater quantity of water, but give up the whole of it with comparative ease.

The Affinity in Intension of the Oxides for Water.

The affinity of the oxides for water in *intension* will be indicated by the temperature required to produce complete dehydration. A careful comparison of these temperatures in the case of the different normal oxides shows that they vary periodically with the atomic weight of the positive element, as seen in the table on p. 95.

In this table, it is found necessary to distinguish between odd and even series. In order to render this distinction more evident, the even series are printed in ordinary type, and the odd series in thick type. Group VIII is omitted, as there are not data to draw any conclusions in regard to it. This table shows—

A. As regards oxides belonging to the same group—

(1.) *That in the case of* odd *members of the same group, the temperature of complete dehydration, and (therefore the affinity of the normal oxides for water),* diminishes *as the atomic weight of the positive element increases.* (There is not a single exception to this rule.)

(2.) *That in the case of* even *members of the same group, the temperature of complete dehydration* increases *as the atomic weight of the positive element increases.*

There is no well-marked exception to this rule, for in the case of ZrO_2 the determination, owing to an accident, was not completed, so that the temperature of complete dehydration might have been higher than that given.

Similar relationships, in so far as the meagre data will allow, are also brought out on comparing the heats of combination of the normal oxides with water in the formation of the hydrates, for example:—Though the temperatures of complete dehydration of calcium, strontium, and barium have not been determined, the heat of combination of the oxides with water shows that they would follow the above rule, thus:—(Compare also Bloxam, *Chem. Soc. Journ.*, **13**, 15; and Smith, *Phil. Mag.* [3], **9**, 87.)

$$\text{Even} \left\{ \begin{array}{l|l} CaO + H_2O = 15500 & \text{thermal units} \\ SrO + H_2O = 17700 & \text{,,} \quad \text{,,} \\ BaO + H_2O = 22300 & \text{,,} \quad \text{,,} \end{array} \right\} \text{(Thomsen).}$$

$$\text{Odd} \left\{ \begin{array}{l|l} P_2O_5 + H_2O = 10700 & \text{thermal units} \\ As_2O_5 + H_2O = 2300 & \text{,,} \quad \text{,,} \\ \text{No data for } Sb_2O_5 \text{ and } Bi_2O_5. & \end{array} \right\}$$

$$\text{Odd} \left\{ \begin{array}{l|l} MgO + H_2O = 3100 & \text{thermal units} \\ ZnO + H_2O = 2700 & \text{,,} \quad \text{,,} \\ CdO + H_2O = 80(?) & \text{,,} \quad \text{,,} \end{array} \right\}$$

So far as oxides of the first and second groups are concerned, it seems as though the temperature of complete dehydration, and therefore the *intensive* affinity of the oxide for water, increases as we pass from the oxide of the element with highest atomic weight in an odd series to the one with the lowest atomic weight, and thence again increases as we pass from the element with lowest atomic weight in an even series to the one with the highest atomic weight; for instance, in the second group we have—

Table showing the Minimum Temperatures of Complete Dehydration of the Metallic Hydroxides by Heat.

Series.	Group I. R_2O.	Group II. $R_2O_2 = 2RO$.	Group III. R_2O_3.	Group IV. $R_2O_4 = 2RO_2$.	Group V. R_2O_5.	Group VI. $R_2O_6 = 2RO_3$.	Group VII. R_2O_7.
1.	**H_2O.**	—	—	—	—	—	—
2.	Li_2O = ?	BeO = high temperature.	B_2O_3 = b. 577°.	CO_2 = b. 100°.	N_2O_5 = affinity for H_2O less than that of P_2O_5; d. at 260° into N_2O_4, O, and H_2O.	—	—
3.	**Na_2O = not at red heat.**	**MgO = 630°.***	**Al_2O_3 = a. 850°.**	**SiO_2 = a. 850°.**	**P_2O_5 = not d. by heat.**	**SO_3 = decomposes on heating.**	**Cl_2O_7 = ?**
4.	K_2O = not at a red heat.	CaO = red heat.	S_2O_5 = ?	TiO_2 = 700°.	V_2O_5 = on evaporation.	CrO_3 = on evaporation.	Mn_2O_7 = ?
5.	**Cu_2O = 360°.**	**ZnO = 585°.***	**Ga_2O_3 = ?**	**GeO_2 = ?**	**As_2O_5 = a. 206°; dull red heat.**	**SeO_3 = not at 265°, at which temperature it decomposes.**	**Br_2O_7 = ?**
6.	Rb_2O = ?	SrO = dull red heat.†	Yt_2O_3 = red heat.	ZrO_2 = about 550° (?)‡	Nb_2O_5 = not at 100°; red heat.	MoO_3 = above 170°.	—
7.	**Ag_2O = about 150°.**	**CdO = 385°.***	**In_2O_3 = 655°.**	**SnO_2 = about 655°.**	**Sb_2O_5 = above 200°, but below redness.**	**TeO_3 = not at 160°, but nearly at a red heat.**	**I_2O_7 = 160°(?)**
8.	Cs_2O = ?	BaO = full red heat.†	La_2O_3 = ?	CeO_2 = about 850°.	Di_2O_5 = ?	—	—
9.	—	—	—	—	—	—	—
10.	—	—	—	—	Ta_2O_5 = low redness.	WO_3 = not at 100°, but on ignition.	—
11.	**Au_2O = below 15°.§**	**HgO = about 175°.**	**Tl_2O_3 = 230°.**	**PbO_2 = about 230°.**	**Bi_2O_5 = 150°.**	—	—
12.	—	—	—	ThO_2 = red heat (?)	—	UO_3 = 300.‖	—

Those of the above data which were not determined by us are taken from *Watts' Dictionary*, *Roscoe and Schorlemmer's Treatise*, and *Gmelin's Handbook*.

* Approximately determined by us.

† Bloxam (*Chem. Soc. Jour.*, **13**, 50), and Smith (*Phil. Mag.* [3], **9**, 87).

‡ An accident prevented the completion of the experiment.

§ That is, it is anhydrous at the ordinary temperature.

‖ Brauner (*Phil. Mag.* [5], **11**, 62).

			Temp. of complete dehydration.	Heat of combination of $RO \cdot H_2O$.
Group II	odd	HgO	175°	?
		CdO	385	80
		ZnO	585	2700
		MgO	630	3100
	even	BeO	high temperature	?
		CaO	above 630°	15500
		SrO	above the temp. for CaO, dull red heat	17700
		BaO	full red heat	22300

B. As regards oxides belonging to the same period or to the same series.*

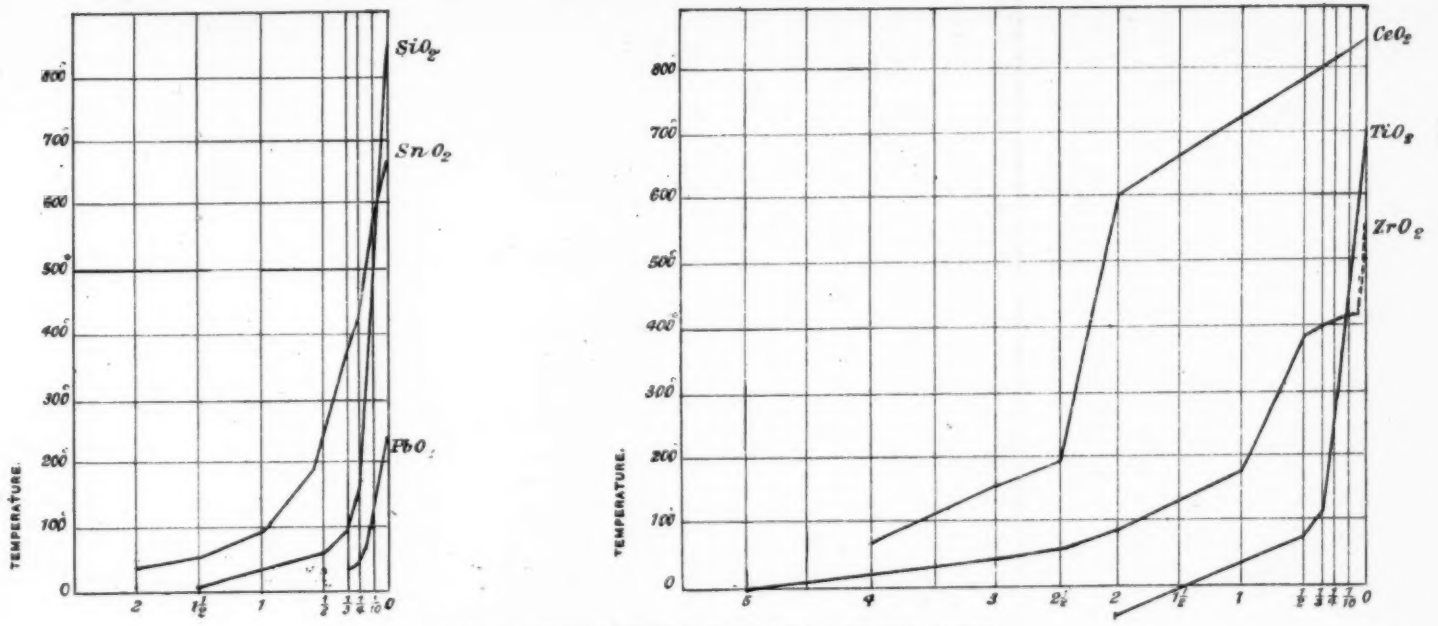
That there is a regular periodic variation of the temperature of complete dehydration with the atomic weights of the elements is quite evident from the table, but the data are not quite decisive as to whether this variation is according to periods or according to series. The data on the whole are more favourable to variation by periods. If this be the case the rule would run thus:—

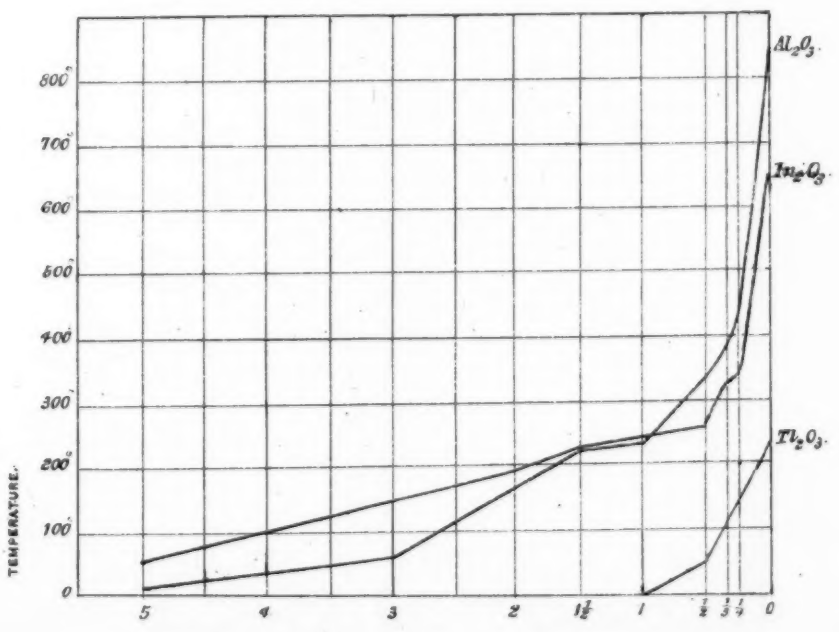
(3.) *For oxides of elements belonging to the same* period, *the temperature of complete dehydration seems to diminish from the beginning to about the middle of the period, and then to increase again to the end of the period,* thus following the same rule as the specific volumes of the elements as represented in Lothar Meyer's curve of the elements, and therefore rising and falling with that curve. The only apparent exceptions are MgO, Bi_2O_5, and possibly I_2O_7, the existence of the last oxide, however, is doubtful.

The very few cases in which the heats of combination of the oxides with water have been determined are in favour of the above form of the rule, thus:—$Na_2O + H_2O = 35600$; $MgO + H_2O = 3100$; $Al_2O_3 + H_2O = ?$; $SiO_2 + H_2O = ?$; $P_2O_5 + H_2O = 10700$; $SO_3 + H_2O = 21300$. If the variation be according to series, instead of according to periods, though this seems less likely, the rule would be:—For oxides of elements belonging to the same series the temperature of complete dehydration increases as we pass from the

* Elements in the same horizontal line belong to the same *series*, so that there are seven in each series. *Periods* are of two kinds: a *short period* contains but seven members, thus from Li to F, and from Na to Cl, are two short periods; a *long period*, on the other hand, embraces 17 members (including Group VIII), thus from K to Br, and from Rb to I, form two long periods, for we have to pass over 16 elements before we come to one, namely, Rb, in which the properties of K are more or less repeated, whereas starting from Li we have to pass over but six elements before we come to Na, or a point at which the properties of Li are in some measure repeated.

DIAGRAM II SHOWING THE NUMBER OF MOLECULES OF WATER RETAINED BY ONE MOLECULE OF AN OXIDE AT DIFFERENT TEMPERATURES.





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beginning (positive end or Group I) to the middle (Group IV) of each series, and then diminishes to the end (negative end or Group VII) of the series.

The exceptions to this form of the rule are more numerous and more serious than those to the form of the rule previously given; they are, P_2O_5, the whole of the oxides of the second series, most probably all the alkaline oxides, and ZrO_2. The temperature given for the last is, however, doubtful for the reasons already stated.

The Affinity in Extension of the Oxides for Water.

Of two oxides belonging to the same group, it does not follow that the one which requires the highest temperature for complete dehydration, and which has therefore the greatest intensive affinity, will also at any other lower temperature combine with the greater quantity of water per molecule of oxide, that is, will have a greater affinity in extension. The very opposite in fact is the case sometimes, though usually the two phenomena run parallel with one another, as will be shown in the following table (p. 98).

From this table, it is seen that in the case of the TiO_2, P_2O_5, and SO_3 groups the order of affinity for water in *extension* is the same as in *intension*, whereas in the SiO_2 and Al_2O_3 groups, so far as the first two members are concerned, the reverse holds good. The last member of each of these groups, however, viz., PbO_2 and Tl_2O_3, follows the same order both in intension and in extension. It is noteworthy that the two corresponding triplets, SiO_2, SnO_2, PbO_2 and Al_2O_3, In_2O_3, Tl_2O_3, of two different groups, are exactly analogous in this respect.

Change of Colour occurring in Dehydration.

Some of the substances in the course of being heated changed their colour (when cold) during a single heating, and when this occurred the loss was always greater than the average before the change. Such a permanent change in colour probably indicated the formation of a definite hydrate or oxide. This change in colour must be carefully distinguished from the temporary alteration in colour which many substances undergo when heated, in which case the change is always towards the red end of the spectrum, as first pointed out by Ackroyd (see *Phil. Mag.* [5], **2**, 423, and *Chem. News*, **34**, 76). Here the original colour is regained on cooling, whereas the changes in colour we refer to are permanent in the cold. The following are the colour changes we have noted :—

Table showing the Temperatures at which one Molecule of the several Oxides of the same Sub-group retains the same number of Molecules of Water.

	No. of molecules of water retained.									
	4.	3.	2.	1½.	1.	½.	⅓.	¼.	⅕.	0.
Al_2O_3	—	62°	172°	220°	242°	337°	372°	427°	480°	abt. 850°
In_2O_3	—	149	192	225	245	264	321	337	400	655
Tl_2O_3	—	—	—		[1]	45	87	113	126	230
	See also Diagram II.									
SiO_2	—	—	—	5	40	61	90	141	243	abt. 850
SnO_2	—	—	39	58	97	252	365	420	470	655
PbO_2	—	—	—	—	—	—	23	39	49	230
	See also Diagram II.									
TiO_2	—	—	—	—	31	71	112	181	340	700
ZrO_2	26	52	88	—	175	375	395	402	408	[550?]
CeO_2	63	153	597	—	731	778	800	809	820	850
	See also Diagram II.									
*P_2O_5	—	160	215	—	red heat	—	—	—	—	not decom.
As_2O_5	15 (?)	100	180	—	206	—	—	—	—	dull red heat
Sb_2O_5	15	—	100	—	175	—	—	—	—	below red heat
Bi_2O_5	—	—	abt. 15	—	—	—	—	—	—	150
*SO_3	—	100	205	—	about 338	—	—	—	—	—
SeO_3	—	—	—	—	about 265	—	—	—	—	—
TeO_3	—	50	—	—	160	—	—	—	—	—

* The data for the last two groups are taken from *Watts' Dictionary* and *Roscoe and Schorlemmer's Treatise.*

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CdO. 300—340°.—Light-brown to dark-brown. Loss 12 per cent.; previous average loss* 4·5 per cent. Indicates change from $Cd(OH)_2$ to CdO.

HgO. 415—440°.—Dirty-yellow to bright-orange. Loss 45 per cent. Indicates change of yellow into red modification of HgO, accompanied by rapid decomposition into Hg and O.

ZrO_2. 385—415°. Grey to white. Loss 4 per cent., previous average loss 0·6 per cent. Due to conversion of $2ZrO_2,H_2O$ into $24ZrO_2,H_2O$ (comp. *Gmelin*, **3**, 342).

SnO_2. 360—385°.—Brownish to pale-yellow. Loss 0·8 per cent., previous average loss 0·26 per cent. Due to conversion of $3SnO_2,H_2O$ to $7SnO_2,2H_2O$.

CeO_2. 585—630°.—Light-yellow to salmon colour. Loss 2 per cent., previous average loss 0·1 per cent. Due to conversion of $CeO_2,2H_2O$ into $CeO_2,(2-b)H_2O$ and finally to CeO_2.

PbO_2. 530—565°.—Brown to yellow. *Loss* 1·8 per cent., previous average *gain* 0·01 per cent. Due to conversion of Pb_3O_4 to PbO.

Tl_2O_3. 585—630°.—Brownish-black to green (fused). Loss 10 per cent., previous average loss 0·4 per cent. Due to partial conversion of Tl_2O_3 to Tl_2O.

Bi_2O_3. 385—415°.—Light-yellow to deep-yellow. Loss 2 per cent., previous average loss 1·3 per cent. Due to conversion of Bi_2O_3,H_2O to Bi_2O_3.

It did not of course follow that for a great loss of weight there was any change in colour.

General Conclusions.

(1.) Precipitated antimony trioxide is anhydrous. On heating, it underwent the following changes:—Sb_2O_3 or $Sb_{20}O_{30}$, stable up to 360°, then rapid absorption of oxygen with formation of $Sb_{20}O_{32}$(?), the latter comparatively stable at 415—440°; then further absorption of oxygen with formation of $Sb_{20}O_{35}$(?), the latter comparatively stable, 500—565°; third absorption of oxygen with formation of Sb_2O_4 or $Sb_{20}O_{40}$, the latter stable from 590° to above 775°.

(2.) The following definite stable hydrates appear to exist:—

(*a.*) AgOH stable up to about 100°, then rapid loss of water with

* That is, during the like interval of temperature immediately preceding the lower limit of the interval in which the colour change was observed.

formation of Ag_2O, (containing a little metallic silver); the latter stable, 180—270°; then reduction to metallic silver, this reduction being complete at 300—340°.

(*b*.) $Hg(OH)_2$ stable up to about 100°; complete dehydration to HgO at about 175°, when incipient decomposition into Hg and O commences, followed by full decomposition at about 415° to 440°.

(*c*.) $CeO_2,2H_2O$ or $Ce(OH)_4$ = orthoceric hydrate; this hydrate was formed on heating precipitated hydrate of cerium dioxide to about 385°. It remained stable from about 385° to 600°. It was of a light yellow colour. On heating to over 600°, it underwent dehydration to CeO_2 and became salmon-coloured. This is the only definite stable hydrate of the oxides RO_2 of the silicon-titanium-group we obtained. In other respects cerium hydrate on dehydration behaved like the hydrates referred to in § 5.

(*d*.) $5Co_2O_3,8H_2O$. This was the composition of air-dried cobaltic hydrate, and was perfectly stable up to 75°.

(3.) The following data with regard to the action of heat on the hydrate of PbO_2 will possibly be of interest in the manufacture of red lead:—Hydrate dried in air = $3PbO_2,H_2O$, complete dehydration at about 230°; PbO_2, stable up to about 280°, loss of oxygen with formation of Pb_2O_3, 280—290°; Pb_2O_3, stable, 290—360°, loss of oxygen with formation of Pb_3O_4, 360—415°; Pb_3O_4, stable, 415—530°, loss of oxygen with formation of PbO at 530—580°; PbO, stable from 580° to above 815°; PbO fused somewhere between 585° and 630°.

(4.) Air-dried thallic hydrate = Tl_2O_3,H_2O, but unstable on heating, complete dehydration to Tl_2O_3 at about 230°; Tl_2O_3, perfectly stable between 230° and 360°, reduction to $3Tl_2O_3,Tl_2O$ at 360—440°; $3Tl_2O_3,Tl_2O$, perfectly stable between 440° and 565°; rapid loss of oxygen and volatilisation of Tl_2O formed at 585—815°; the rate of loss gradually diminishing after fusion at 630°; remaining Tl_2O_3 constant from 815° upwards.

(5.) An examination of all the results shows that, with the exceptions referred to in § 2, there is no certain indication of the formation of definite hydrates which are stable through any but possibly a very small range of temperature (less than about 13°). From this we must conclude either that there are no definite hydrates formed on heating at gradually increasing temperatures, or that a very large number of such hydrates are produced under these conditions, but are so unstable that a further small rise in temperature is sufficient to convert a higher into a lower hydrate. Of these the second alternative is, for reasons given, by far the more probable.

Our results accord entirely with Henry's theory that the known metallic oxides are polymerides $n(RO_x)$ of the unknown simple oxides RO_x. The results also show that in most cases, especially those of

SiO_2, TiO_2, SnO_2, Al_2O_3, &c., the coefficient n of polymerisation must be very large, as might be expected from the infusible character of these oxides. Minimum values for this coefficient are indicated in some cases.

(6.) The retention of water by many oxides at comparatively high temperatures, at and above a red heat, is noteworthy. This is especially interesting in the case of the hydrate of cerium dioxide, $Ce(OH)_4$, which is stable to as high a temperature as 600°. The retention of water at such high temperatures illustrates the great importance in quantitative analysis of the thorough ignition of the hydrates in order to drive out the last traces of water before weighing.

(7.) The minimum temperature of complete dehydration is a periodic function of the atomic weight, as follows:—

(*a.*) *For normal oxides of* odd *members of the same group, the minimum temperature of complete dehydration diminishes as the atomic weight of the positive element increases.* (No exception.)

(*b.*) *For* even *members of the same group it increases as the atomic weight of the positive element increases.* (No well-marked exceptions.)

(*c.*) *For normal oxides of elements belonging to the same* period, *the minimum temperature of complete dehydration diminishes from the beginning to the middle, and then increases to the end of the period.* The only apparent exceptions are MgO, Bi_2O_5, and I_2O_7 (?).

These results also accord with the heats of combination of the normal oxides with water in the formation of hydrates.

(8.) Of two oxides belonging to the same group, the one which requires the highest temperature for complete dehydration will usually combine at any other lower temperature with a greater quantity of water per molecule of oxide; this, however, is not always the case, the pairs SiO_2,SnO_2 and Al_2O_3,In_2O_3 being marked exceptions. From this we may conclude that the order of affinity of the oxides for water is usually the same both in intension and in extension, though not always.

(9.) Changes of colour on dehydration, which are *permanent on cooling*, usually indicate the formation of a definite hydrate, or that the dehydration is complete, or that some other definite chemical change has occurred.

V.—*Note on a Modification of Traube's "Capillarimeter."*

By H. S. Elsworthy.

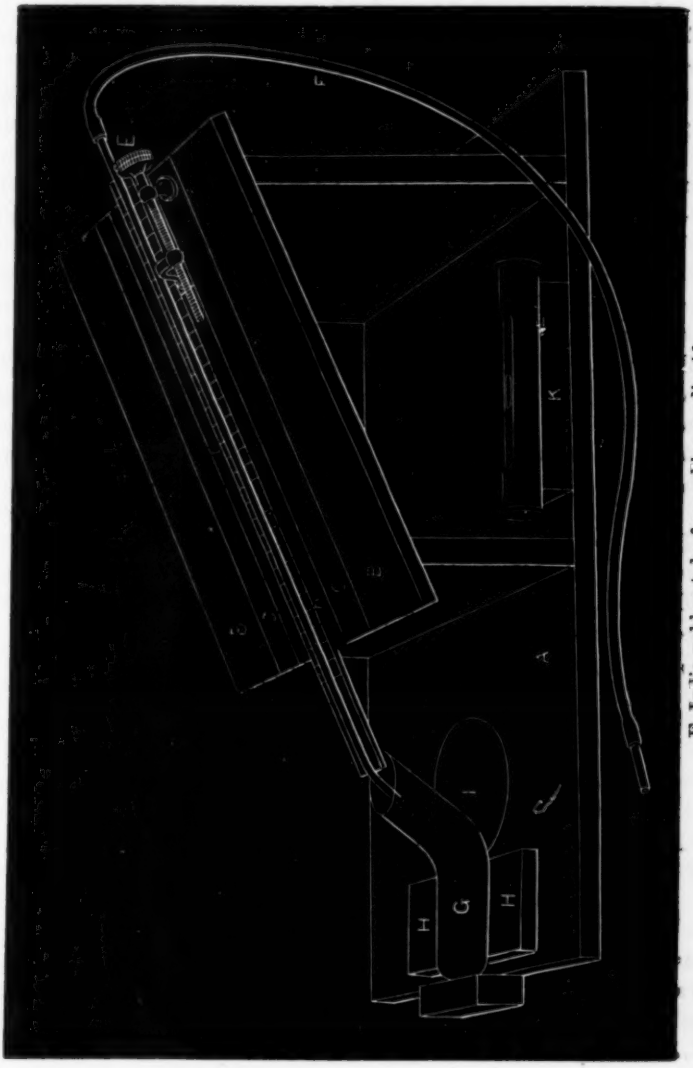
Having a number of native Indian liquors to analyse, especially with regard to the amount of fusel oil contained in them, I determined to try the capillarimetric method proposed by J. Traube in the *Zeit. für Spirit Ind.*, No. 36 of 1886, this being according to the author both the quickest, least costly, and most accurate method, especially for small proportions of fusel.

Not having the apparatus, and there being no time to obtain it from Germany, I attempted to make one from a broken thermometer having a thin-walled capillary tube, and the scale of which was divided pretty accurately into 1·12 mm., that is, 88·5° equalled 100 mm. On testing this, I found that a 20 per cent. (vol.) solution of pure alcohol rose to a height of 76°, and that 0·1 per cent. of fusel oil depressed the height by very nearly 1°. It was, therefore, possible to read to $\frac{1}{50}$ per cent., as claimed by Traube, but it was, as might be expected, rather difficult, and the scale had to be adjusted to the surface of the liquid with the greatest nicety.

On thinking over the matter, I concluded that if the tube were laid at an angle approaching the horizontal, the height to which the liquid would rise would be correspondingly increased.

I therefore made an apparatus as follows: a broken milk scale thermometer, graduated up to 600° F., furnished the required capillary tube. The divisions on the scale very nearly corresponded with 1 mm., that is, 151° equalled 150 mm. On a stand, A, about 15 inches long, is placed a sloping piece of wood, B, the lower end of which is raised 2 inches above the stand, and slants upwards at an angle of 10°. In the centre of this inclined plane, a piece of wood, D, is made to slide easily between two other strips, CC, and to this is attached the scale and capillary tube, the end of the latter being slightly bent downwards. The slide can be adjusted by a screw, E, so as to bring the lower end of the scale in exact contact with the surface of the liquid. On the stand, near the lower end of the inclined plane, is placed a piece of glass tube, G, bent to a convenient angle, and ground off level, this being filled with the spirit to be tested. This tube is fixed moderately firmly between two small cork blocks, HH. The scale must be adjusted accurately to the same point each time, and this is effected by bringing the lower end of the scale itself, or a point attached to it, into exact contact with the surface of the liquid. This may be done with the greatest nicety by placing a polished

metal or glass reflector, I, under the bent portion of the glass tube when the exact moment of contact can be easily observed; without



F, India-rubber tube for sucking up liquid.

the reflector it is difficult to adjust it properly. The stand should be set exactly level by means of a spirit-level, K, and an adjusting screw.

By attaching an india-rubber tube, F, to the upper end of the capillary tube, it is easy to suck the liquid up the tube, or force it

back, and it is also used for cleaning the apparatus with pure spirit, and for sending dry air through afterwards.

I find that the most accurate readings can be obtained by drawing the liquid up the tube five or six times, and finally to a fixed point some 10° or 20° above the point reached by pure spirit.

In Traube's instrument the rise of a pure 20 per cent. vol. spirit is said to be 50 mm. In the modification here proposed a pure spirit rises 173 mm., and with 1 per cent. of fusel oil the meniscus is lowered 25 mm. against 7 mm. in the former apparatus. The instrument described is therefore more than three times as sensitive as Traube's.

From my experience with this apparatus, I find that it is necessary to distil the spirit under examination with soda or potash in order to eliminate the ethers, which have a very considerable influence on the capillary rise. One drawback is the amount of dilution required by, say, a proof spirit. If, for instance, the original liquid was proof, and contained 0·1 per cent. of fusel oil, it would require approximately one and a half times its volume of water, and the percentage of fusel oil in the mixture would be correspondingly lowered.

It is quite possible that a stronger spirit may answer the purpose, but I have not as yet had time to try it.

It seems to me that the experiments I have already made fully bear out Dr. Traube's recommendation, and the use of the capillarimetric method will tend to greater accuracy in the estimation of fusel oil than has hitherto been possible.

VI.—*The Constitution of the Copper-Zinc and Copper-Tin Alloys.*

By A. P. Laurie, B.A., B.Sc.

If instead of a simple metal, a mixture of two metals is introduced into a voltaic cell, the E.M.F. of the cell is that of the more positive metal. For instance, a mixture of zinc and copper will give the E.M.F. of zinc.

Several experiments in a cuprous iodide cell with plates of copper having pieces of zinc soldered into them of about $\frac{1}{2000}$ of the whole area of the plate, showed this. On first connecting with the electrometer, the deflection was about half that for zinc (the deflection for copper being of course zero), but it gradually crept up, ultimately attaining a value some 4 or 5 hundredths of a volt below the value

for zinc. This gradual increase of E.M.F. was due to some change in the electrical condition of the compound plate, and is probably to be explained by the gradual polarisation of the copper plate by the local action between it and the zinc soldered on to it. But, in whatever way these points are explained, the results are sufficient to show that a mixture of two metals gives the E.M.F. of the more positive metal, and that this holds good as long as at least 0·2 per cent. of the positive metal is present.

If, however, in place of a mixture of zinc and copper we have an alloy of the two metals which has been formed with a development of heat, and which therefore is of the nature of a chemical compound, the result will probably be different, for it is obvious that the dissolution of the zinc will in this case necessitate the decomposition of this zinc-copper compound, whereby energy is absorbed, and therefore the E.M.F. of the cell will probably be correspondingly lowered.

Now there are three possible ways in which zinc-copper alloys may be constituted.

First, they may be merely mixtures of zinc and copper; in that case they would give the E.M.F. of zinc in the voltaic cell.

Second, they may be of the nature of the solution of sulphuric acid in water; in that case, a series of such alloys, beginning with 100 per cent. of copper and ending with 100 per cent. of zinc, would probably show a gradual rise of E.M.F. in the cell, from the value for copper to that for zinc.

Third, one or more of the series of alloys may be a definite atomic compound, the rest being solutions of this compound or compounds in an excess of zinc or copper; in that case the E.M.F. would probably rise by a jump when a series of alloys were tested, a slight excess of zinc over that necessary for the compound causing a great alteration of E.M.F. in the cell. Further, this jump would probably occur where the percentages of zinc and copper corresponded with some simple molecular formula.

In practice, the difficulty which presents itself is that of obtaining homogeneous alloys. This difficulty can only be overcome by taking great care in their preparation, and by preparing very large numbers of them. In this way, any error from this cause may be expected to show itself.

My zinc-copper alloys were prepared as follows:—

A certain quantity of copper and of zinc were weighed out, amounting together to about $\frac{3}{4}$ of an oz., and fused in a Fletcher's furnace under borax; when fused, the alloy was vigorously stirred with an iron rod coated with borax, and poured instantly into a little trough cut in a block of charcoal. The ingot thus formed was cooled,

weighed, and then broken across; if it seemed homogeneous in section the upper layer was filed off, the ingot marked, and laid aside for testing by the electrometer. Some zinc always burned off, and the percentage of zinc and copper was calculated from the weight of copper taken and from the weight of the alloy obtained; this, of course, assumes that there is no loss of copper—in fact it is but very slight, and also necessitates clean casting, which is easily managed if the flux is sufficiently fluid. The stirring was always kept up till the last instant before emptying the crucible. The alloys corresponded in appearance to the descriptions already published, the yellow tough "brass" being replaced by white brittle alloys when the copper was diminished below 50 per cent., and these again giving place to hard grey alloys when it was below about 15 per cent.

On testing a piece of brass wire in the cell it gave no deflection, showing a diminution of E.M.F. = 0·6 volt. It probably contained about 30 per cent. of zinc. One of my alloys containing about 25 per cent. of zinc gave the same result. As 40 per cent. of copper was approached, a slight increase of E.M.F. showed itself amounting at 36 per cent. of copper to about 0·1 volt; so that from nothing up to 66 per cent. of zinc the E.M.F. had gradually risen about 0·1 volt.

The next alloy tested contained about 33 per cent. of copper. It gave a deflection of about 0·5 volt. All the alloys containing less than this amount of copper, though varying a good deal, continued on this higher level of E.M.F. The results are given in detail in Table A (p. 107) and Plate 4 (p. 116).

The want of homogeneity of the alloys is brought out by this table, but at the same time is not sufficient in any way to conceal the striking shape of the curve of E.M.F. showing its sudden rise. It is to be remembered that although the alloys may have an average composition very close to that given in the table, the electrometer will select the portions of the alloy containing an excess of zinc. These experiments indicate, in the first place, a considerable development of heat in the formation of brass, lowering the E.M.F. of the cell about 0·6 volt, and, further, that the greater part of this development of heat is due to the formation of a compound $CuZn_2$ (32·8 per cent. Cu).

After these experiments were completed, I determined to test whether the zinc-copper alloys could be separated by differences in their specific gravity.

For this purpose, imitating Matthiessen's experiment, I raised a porous pot, about 3 in. high by $\frac{5}{8}$ in. across, to a bright red in a Fletcher's furnace, and poured into it an alloy containing a little over 34 per cent. of copper. The furnace being again closed, and the

TABLE A.—*Zinc copper Alloys.*

Percentage of copper.	E.M.F. in volts.
100·0	−0·020
75·0	−0·020
54·4	+0·040
50·5	0·070
49·3	0·070
47·2	0·075
46·1	0·065
43·9	0·070
41·7	0·080
37·0	0·085
36·5	0·085
35·9	0·160
33·8	0·530
33·2	0·520
31·9	0·540
31·9	0·580
30·3	0·570
29·2	0·600
28·0	0·580
26·8	0·490
26·2	0·460
25·7	0·570
24·3	0·475
23·0	0·600
19·1	0·580
18·7	0·420
16·4	0·580
16·2	0·580
14·5	0·590
14·1	0·580
12·4	0·590
12·1	0·600
3·5	0·590
Zinc.	0·600

blast kept on, the alloy was kept fused for at least 30 minutes. It was then allowed to cool, the porous pot broken, and the cylinder of alloy, after it had been filed flat on one side, was connected with the electrometer, and gradually lowered into the cell.

If there had been any regular settling out of alloys according to specific gravity, one end should have had a higher E.M.F. than the other. If, then, the end of lowest E.M.F. was first plunged in the liquid, its gradual immersion would cause an increase of the deflection on the scale. No such effect was produced, however, for no matter which end was first plunged in, the E.M.F. continued at about 0·1 volt, varying slightly. The same alloy, fused up with fresh zinc

to reduce the percentage of copper to about 20 per cent., gave all along its length an E.M.F. of about 0·5 volt, varying slightly. There is therefore no serious want of homogeneity produced by differences of specific gravity. All these experiments tend to confirm the trustworthiness of the results first obtained.

As the slow cooling in an upright position seemed to have no injurious effect, six alloys were made up, of about 2 oz. each, and cast in moulder's earth in an upright position as sticks about 2 in. long and $\frac{5}{8}$ in. in diameter. A portion about 1 in. long was broken from each of these sticks by knocking off the two ends; it was then filed flat on one side and plunged into the cell. The results with these six sticks are given in Table B. It will be noticed that, with one exception, the deflections increase as the zinc increases with considerable regularity. They are evidently more homogeneous than the first set of alloys.

My next experiment was as follows. Taking alloy No. 6 of the set in Table B, I ground it to powder, and tested its E.M.F. by packing it into a minute glass vessel, shaped like a tobacco pipe, with a platinum wire down the stem and into the bowl, this bowl being plunged beneath the liquid in the cell. It gave an E.M.F. of about 0·5 volt, but as the experiment failed unless the dust was wet and carefully packed, no deflection being obtained, I next filled the bowl with mercury, mixed in some of the dust, and obtained again an E.M.F. of about 0·5 volt. Some of this dust was next treated with dilute sulphuric acid; hydrogen was given off, but after boiling for some time with the acid all effervescence ceased, or almost ceased, although fresh acid was put on. The acid contained some zinc, but no copper. On burnishing the dust, it gave the same bright white lustre as before. The dust when introduced into the bowl of the glass pipe, both with and without mercury, gave the deflection of about 0·08 volt, so that apparently the excess of zinc had been removed by the acid.

TABLE B.

Percentage of copper.	E.M.F. in volts.
34·1	0·160
31·5	0·420
31·0	0·560
30·6	0·480
30·1	0·530
29·9	0·570

These results certainly indicate the existence of a compound, $CuZn_2$, the sudden rise of E.M.F. being difficult to interpret in any other way, and seemed to me sufficiently encouraging. At the same

time the zinc-copper alloys, and especially those containing a high percentage of zinc, are difficult of preparation, and very little is known about their physical properties. It seemed better, therefore, to select for further experiments some well-known series of alloys, in order to check the results of this new method against the conclusions of other experimentalists. For this purpose, the tin-copper alloys seemed especially suitable.

In the first place, Riche (*Compt. rend.*, **55**, 1862) states that the curve of densities for these alloys has two maxima, corresponding respectively with the alloys Cu_4Sn and Cu_3Sn. The curve of densities given in Thurston's Report* on the copper-tin alloys, though not showing two maxima, rises to a maximum over the region of these two alloys, falling off towards copper and towards tin. Riche further states that these two alloys alone are not subject to liquation.

Matthiessen (*Phil. Trans.*, 1860) failed to find any indication of the existence of these compounds on testing the electric conductivity of these alloys, but this has been shown by Lodge to be due to his not having investigated that portion of the curve. Lodge (*Phil. Mag.*, 1879) finds a minimum conductivity at Cu_4Sn, and a maximum conductivity at Cu_3Sn. Again, the curve for heat conductivity given by Calvert and Johnson (*Phil. Trans.*, 1858), shows a minimum at Cu_4Sn, and maximum at Cu_3Sn. Finally, the induction balance curve as determined by Roberts-Austen (*Phil. Mag.*, 1879), shows the same maximum and minimum. There is consequently a considerable amount of evidence pointing to the existence of the compounds Cu_3Sn and Cu_4Sn in this series of alloys, a mass of evidence first, I believe, collected and pointed out by Roberts-Austen. These alloys, therefore, seemed to be peculiarly suitable for testing the new method. The compound Cu_4Sn I did not expect to find, but the compound Cu_3Sn would in all probability be indicated. In the first place, however, I thought it best to again test the behaviour of compound plates, adopting a different arrangement.

A Daniell cell was constructed containing a large cylindrical copper plate, coated with india-rubber on the back, and with a front surface of 500 sq. cm. This plate was placed in a solution of sulphate of zinc. A glass tube plugged with plaster of Paris, and containing a copper wire in a solution of sulphate of copper, formed the other pole of the cell. This wire was connected permanently to the electrometer. A thin strip of zinc, of breadth 5 mm., was arranged so that it could be covered to any depth in the solution. Either the zinc plate, or the copper plate, or both, could be connected to the electrometer by means of mercury cups. The copper plate was first

* Report on Copper-Tin Alloys, United States Board, to test iron, steel, &c.: Washington, 1879.

connected. It gave a small deflection of about 0·03 volt. The zinc plate was then immersed in the solution to the depth of 5 mm., and then connected by a wire to the copper plate; immediately the spot of light on the scale began to move, and time observations were taken. The results are plotted on Plate 1 (p. 116). The deflection for the zinc alone is also marked on the curve. On disconnecting the zinc plate, the spot of light moved steadily down to the old deflection for copper alone, an appreciable time elapsing before the polarisation of the copper plate ceased. The zinc on removal was found to be corroded, a considerable amount of zinc having been consumed in polarising the copper plate. Similar experiments were made with a cell containing an acid solution of stannous chloride, and a copper wire coated with cuprous chloride for the other pole. In this case also a similar curve was obtained on connecting a tin plate to the copper plate in the same way. In both cases, the surface of the positive metal amounted to about $\frac{1}{1000}$ part of the surface of the copper plate. No experiments were made to test the effect of distributing the tin over the copper surface, though I am disposed to think that this would probably increase the rate at which the plate becomes completely polarised. These experiments seem to me to open out an interesting method of investigating polarisation. By weighing the zinc before and after, some light might be thrown on the thickness of the molecular layer necessary to polarise the copper plate, but I did not wait to make any such experiments. If, then, one of our tin-copper alloys contained only 0·1 per cent. of its surface of tin merely mixed with it, we might hope to detect it on the electrometer.

Preparation of the Alloys.

The alloys were prepared from the best grain tin and the best copper, 99·9 per cent., obtained from Johnson and Matthey's. A weighed quantity of copper was in each case melted in a plumbago crucible under charcoal, hydrogen bubbled through it to be sure of the absence of suboxide, removed from the furnace, a weighed quantity of tin rapidly added and thoroughly mixed, and the alloy poured into an open mould. The casting formed a cylinder about 13 cm. long by 0·8 cm. diameter. The aggregate weight of tin and copper was 100 grams. Prof. Roberts-Austen kindly allowed these alloys to be prepared with the assistance of Mr. Groves at the Royal Mint. They had thus the advantage of being made by one skilled in the melting and mixing of metals. They had all a fine appearance on fracture.

The alloys prepared were as follows:—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
Cu per cent.....	100	95	90	85	80	75	70	68·18

	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)
Cu per cent.....	67	64	61·64	60	40	0

8 and 11 correspond to the two supposed compounds, Cu_3Sn and Cu_4Sn.

Subsequently a fresh set of alloys were prepared of the following percentage composition :—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Tin per cent.....	37	38	39	40	41	42

It was thought advisable to analyse certain of those alloys that were shown to be of especial importance in the ultimate results. These analyses agreed pretty closely with their supposed composition.

Alloy 11 was found to contain 61·7 of copper.

Alloy 12, analysed at both ends, was found to contain 60·4—60·6 per cent. of copper.

Alloy of 39 per cent. in the second series was found to contain 61·2 of copper.

The Cells used.

The cells used consisted either of a solution of stannous chloride and a copper wire coated with cuprous chloride, or of stannous sulphate and a copper wire within a porous partition containing copper sulphate. Such tin cells have been carefully tested and found to yield a definite E.M.F. (*Phil. Mag.*, 1886 [5], **21**, 13).

Experiments with the Electrometer.

I first determined to test all the alloys in succession in a solution of stannous chloride acidified with hydrochloric acid. The composition of the solution was as follows : $SnCl_2$ 33 grams, water 1750 c.c., strong pure hydrochloric acid 17·5 c.c. The cell consisted of a shallow glass dish, with a wooden cover drilled full of holes, through each of which one of the sticks could be dropped, and its E.M.F. tested by the electrometer ; in this way, all the alloys were tested under exactly similar conditions. The other pole of the cell consisted of a copper wire coated with cuprous chloride.

The results of the first set of observations in which the rods were polished with emery paper, and then immersed, are shown in Curve (*a*), Plate 2, which gives the mean of this and the next two methods of testing the alloys. The numbers thus given are the mean of two or three independent sets of observations. In the first place, the sudden

rise in E.M.F. on passing Cu_3Sn will be noticed. No corresponding effect is observable on passing Cu_4Sn, but the alloys give slightly irregular deflections in the cell, as shown by the zigzag of the line joining the observations. The irregular numbers are probably due to ephemeral causes, the metals not entering into the action of the cell, and consequently coatings of gas, &c., producing variable deflections, as has been noticed in the case of platinum plates.

Certain precautions are necessary in order to get trustworthy and uniform results in experiments of this kind. In the first place, the cell used should be so designed as to give a definite E.M.F., free from polarisation effects, such as the Daniell, cuprous chloride, or iodine cell. In the second place, the solution in which the alloys are placed should not directly attack the metals in the alloy. In the third place, the salt used should be a salt of the more positive metal. For instance, I have failed to obtain constant results from a cell containing common salt in place of stannous chloride, no doubt due to gas, polarisation of the alloy, complex secondary actions, &c. In the fourth place, the alloys must always be carefully cleaned with fresh emery paper before being plunged in the solution. With the electrometer, internal resistance can be ignored, and many arrangements of cells are consequently available. For instance, I sometimes place the inner solution in a glass tube drawn out to a fine capillary, or sometimes use as my cell a U tube, constricted at the bottom and plugged with plaster of Paris.

With reference to alloy 12, at which the rise occurs, two points are worthy of notice. First the rise is instantaneous, there is no creeping up of E.M.F., as in the case of the compound plates described before. This is probably due to the distribution of the free tin all over the surface of the alloy instead of being located at one point. The next point is, that in about 10 or 15 minutes the deflection disappeared. This can easily be accounted for by supposing the free tin to exist in pockets and not in veins; these pockets would soon be consumed by the local action, and the E.M.F. would then fall. One confirmation of this is the fact that it is only necessary to reburnish the surface with emery to restore the original E.M.F. Some additional facts favouring this view will be mentioned presently. It is of some interest to note the actual surface of free tin to which the deflection is probably due. If we suppose 1 c.c. of the alloy to be immersed in the solution, then the whole area of the rod present, leaving out the end, amounts to about 2·5 sq. cm. If we suppose the alloy to contain 1 per cent. of tin evenly distributed over the surface, this gives 0·025 sq. cm. as the actual surface of tin in action.

The E.M.F. of the alloys were next tested in a solution of stannous chloride containing no free acid. The results are given in Curve (*a*),

Plate 2. The only difference noticed here was the very gradual disappearance of the deflection of 12, the E.M.F. remaining practically the same for an hour.

The polished surface of the alloys having thus been tested, they were next broken across the centre, and the broken ends plunged in the solution. The results are given in Curve (*a*), Plate 2.

The next experiment was to test the effects of amalgamation. Alloy 11 and alloy 12 were both amalgamated. The E.M.F. were respectively 0·008 volt and 0·26 volt. The only difference caused by amalgamation was that the deflection given by alloy 12 was now permanent. This is of interest, as confirming the view taken of the condition of the free tin on the surface. The mercury doubtless eats into the alloy, and dissolving the tin, brings it to the surface. It will also tend to check the violence of the local action. It is also curious to note that the alloy 11 is not affected by amalgamation, and that consequently the compound is seemingly unaffected by solution in mercury.

The alloys were next tested in a cell consisting of stannous sulphate in acid solution, and copper sulphate round a copper wire, divided by a porous partition. The results are given in Curve (*b*), Plate 2. They are the mean of two distinct sets of observations. It will be noted that a distinct deflection is given by all the alloys.

Alloys of the second series were now prepared and tested. The results obtained were the same and have not therefore been plotted. The alloys were all amalgamated.

One alloy however behaved differently, namely, 3. This alloy gave uncertain values, sometimes high, sometimes low. If the results of the two groups of alloys are compared together we find that—

1st series, alloy containing 38·3 per cent. tin gives the low deflection 0·008 volt.

2nd series, alloy containing 38·8 per cent. gives an irregular deflection.

1st series, alloy containing 39·5 per cent. gives a definite but vanishing deflection, 0·26 volt.

2nd series, alloy containing 40 per cent. (not analysed) does the same.

2nd series, alloy containing 41 per cent. (not analysed) gives a permanent high deflection.

2nd series, alloy containing 42 per cent. (not analysed) gives a permanent deflection.

It will be noticed how closely their percentage compositions and their behaviour on the electrometer agree.

Having completed these measurements, I next searched carefully for Cu_4Sn by two methods. In the first place, I used a cell in which

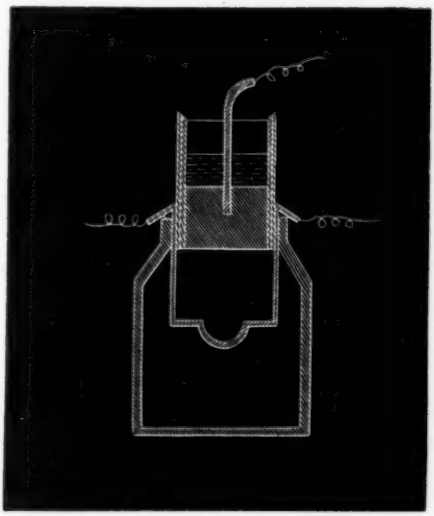
copper gave a definite E.M.F. as well as tin, so as to get rid of the small irregular deflections noticed in the former cells. For this purpose silver and sulphate of silver were substituted for the copper and sulphate of copper. In this cell, copper gave a deflection of 0·482 volt, and tin of 0·965 volt, consequently a considerable deflection for copper was combined with a marked difference of E.M.F. between copper and tin. There was no indication here of a Cu_4Sn compound, the E.M.F. not rising in two jumps but only one. The second method was to use a cell in which copper gave a large deflection, but in which the difference between copper and tin was small. Here I hoped that in the region between Cu_4Sn and Cu_3Sn the curve would dip, owing to the necessity of decomposing the mixture of the two compounds. No indications of this have been obtained, as the following figures show:—

Copper, 0·56 volt; alloy 5, 0·55 volt; alloy 10, 0·60 volt; tin, 0·73 volt. The cell used was an iodine cell.

These experiments complete the work with the electrometer. I next experimented on the possibility of eating out the free tin from an alloy by placing it in the cuprous chloride cell and short circuiting. If the electrometer results were trustworthy, an alloy containing an excess of tin over Cu_3Sn would be attacked when used in place of the zinc plate in such a cell, until the excess of tin had been removed. The E.M.F. would then fall practically to zero and all action would stop, Cu_3Sn remaining unaffected. For this purpose, I selected alloy 13 (60 per cent. tin), and cast it into a thin plate about 1 in. × 2 in. × $\frac{1}{16}$ in. thick. This was placed in acid stannous chloride, and connected with a copper plate in a paste of cuprous chloride inside a porous pot. After two or three days all action seemed to stop, and the plate, under the microscope, in place of having a rough but homogeneous surface, seemed made of bundles of needle-shaped crystals with cavities between. It had not, however, been eaten through, only a thin outer layer having been affected. This outer layer, on being scraped off and analysed, was found to contain 45 per cent. of tin. These results being indefinite, a cell was next constructed in which the finely-powdered alloy could be attacked. Another point attended to was making the cell air-tight, so as to prevent oxidation of the cuprous chloride, and its partial solution, diffusion, and deposition as metallic copper on the alloy. The following diagram (p. 115) shows the cell used.

This consists of a wide-mouthed 1 oz. bottle, containing acid solution of stannous chloride; in this solution, is plunged a copper cup supported by two copper strips. A weighed quantity of the finely-powdered alloy is placed in this cup, and covered with a disc of linen to keep out possible impurities. The bottle is then corked

by a glass tube covered at the end with parchment paper, and containing a paste of cuprous chloride and a copper plate, the whole being filled up with paraffin; after pushing in the glass tube, paraffin is poured round the neck of the bottle. The powdered sample of alloy taken was found to contain on analysis 36·4 per cent. of tin. The



current from the cell was allowed to flow through a little copper voltameter, the plates of which were occasionally weighed; after 36 hours, the plates no longer increasing in weight, the alloy was removed and analysed; it still contained 44 per cent. of tin, so that this experiment was not very successful. A second supply of alloy was again placed in the cup, and the cell connected to the voltameter. The time curve of the voltameter is given on Plate 3. When the curve had reached the point (*a*) the alloy was removed from the copper cup, re-ground in an agate mortar, and replaced in the cup; immediately the current took a fresh start, as is shown by the curve. When the curve had reached (*b*), the alloy was again removed, ground, and put back; this time very little additional tin was removed, and the alloy was therefore considered fit for analysis. On weighing the residual alloy and calculating the tin lost, the alloy apparently contained 38 per cent. of tin. On analysis, it was found to contain 41·2 per cent. of tin. Evidently, then, this residual alloy agrees pretty closely in composition with the compound Cu_3Sn. The difficulty evidently is to remove the last traces of free tin inclosed in portions of the alloy, the re-grinding enabling this to be more com-

pletely done. On putting alloy 11 in the copper cup for 36 hours, no change or indication of electric current could be detected.

These experiments, therefore, afford strong evidence that Cu_3Sn is a compound of definite formula and considerable heat of formation, thus confirming the evidence obtained by other methods. It remains to apply the method to less known alloys, with the view of throwing light on their constitution.

VII.—*An Extension of Mendeléeff's Theory of Solution to the Discussion of the Electrical Conductivity of Aqueous Solutions.*

By Holland Crompton, Student in the Chemical Department of the City and Guilds of London Central Institution.

As a consequence of Mendeléeff's original treatment of the subject, our conceptions of the constitution of solutions have suddenly acquired a degree of precision which is altogether remarkable when the nature of the problem is considered. Fellows of the Chemical Society have had the privilege to be put in direct possession of the views of the renowned Russian chemist, his method of treating the problem being briefly indicated in a paper on "The Compounds of Ethyl Alcohol with Water" in the October number of the *Transactions* (1887, p. 778). By discussing the dependence of change of relative density on percentage composition, Mendeléeff arrives at the conclusion that three distinct hydrates of alcohol may exist in solution in a dissociated condition—$C_2H_6O{\cdot}12OH_2$, $C_2H_6O{\cdot}3OH_2$ and $3C_2H_6O{\cdot}OH_2$; and the reliability of his method is established to demonstration by his success in isolating the first and second of these. Discussing the data for sulphuric acid in a similar manner (Ostwald and Van't Hoff's, *Zeit. phys. Chem.*, 1887, 273), he concludes that this acid forms the hydrates—

$$H_2SO_4{\cdot}OH_2 \quad H_2SO_4{\cdot}2OH_2 \quad H_2SO_4{\cdot}6OH_2 \quad H_2SO_4{\cdot}150OH_2,*$$

the existence of two of which is already recognised by chemists.

It is evident and was pointed out by Mendeléeff in the paper in which he first advanced his views of solution (*Ber.*, 1886, 379), that the presence of the hydrates thus indicated must influence other physical properties as well as that of density, and the problem therefore is one of determining in what manner and to what extent this

* See Dr. Armstrong's remarks regarding this "hydrate."

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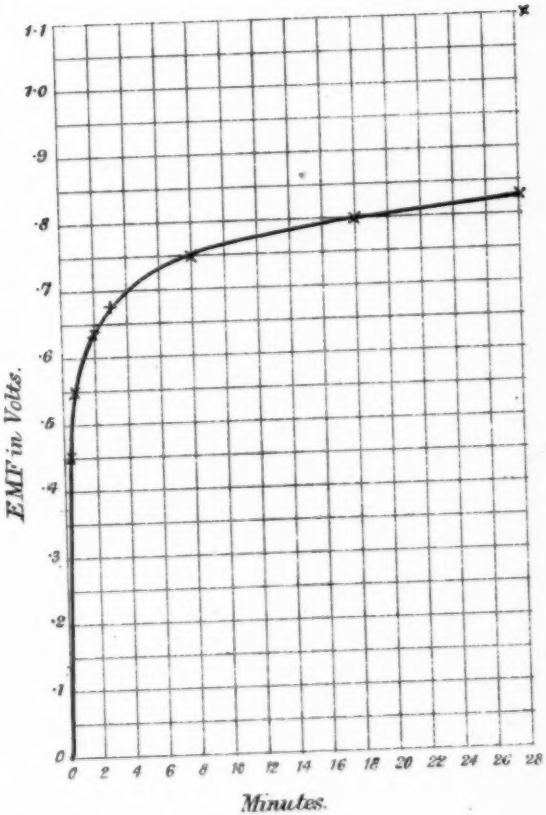

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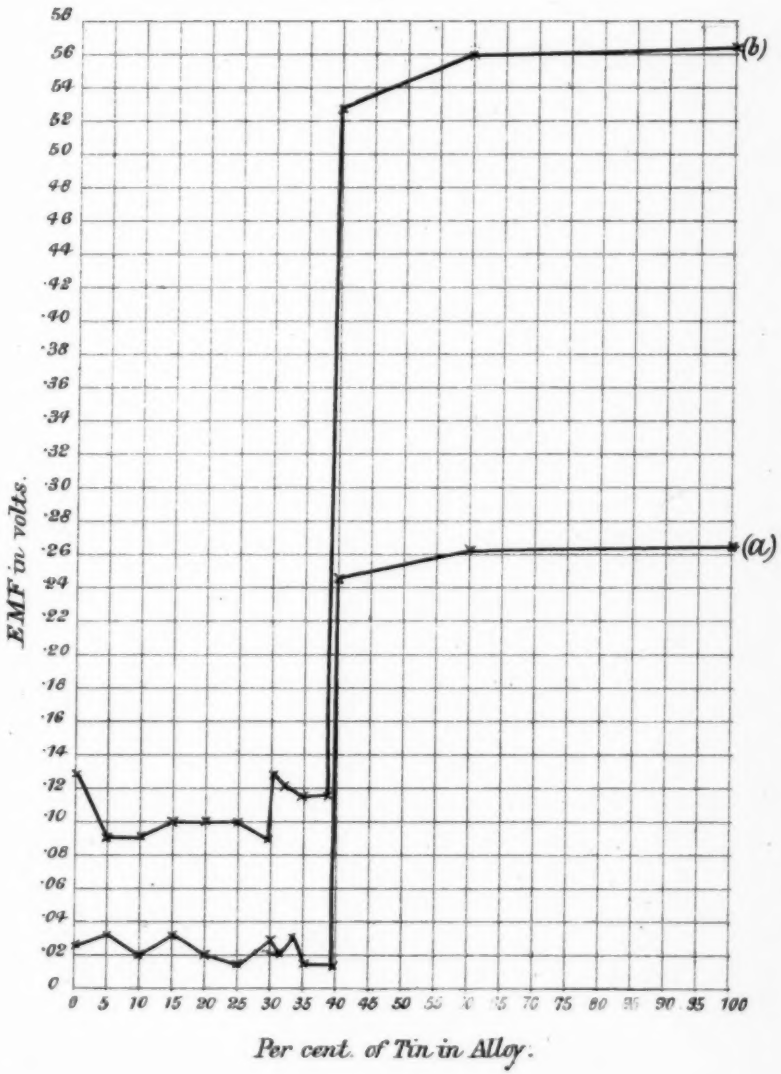
E. M. F OF ALLOYS (A) IN STANNOUS CHLORIDE.
(B) IN STANNOUS SULPHATE.



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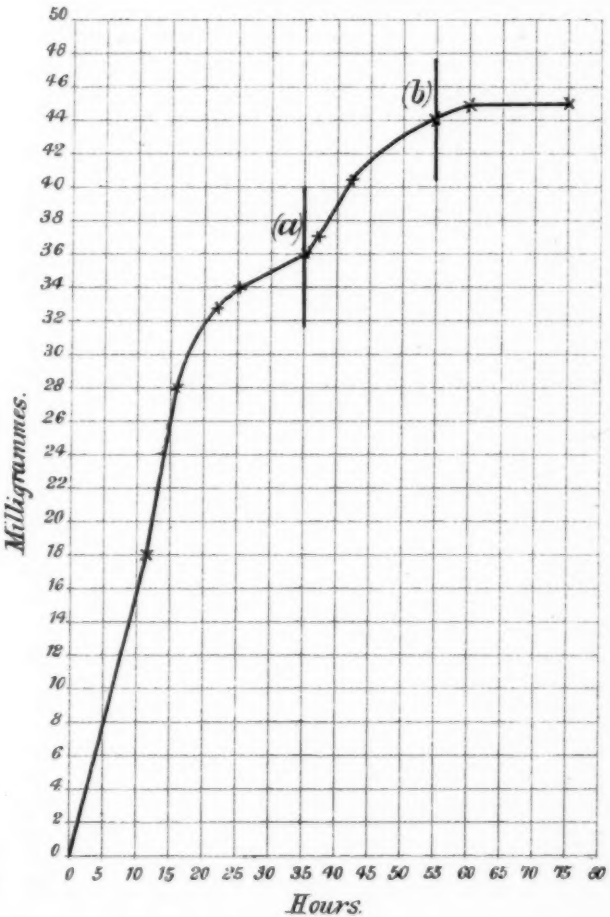
VOLTAMETER CURVE.



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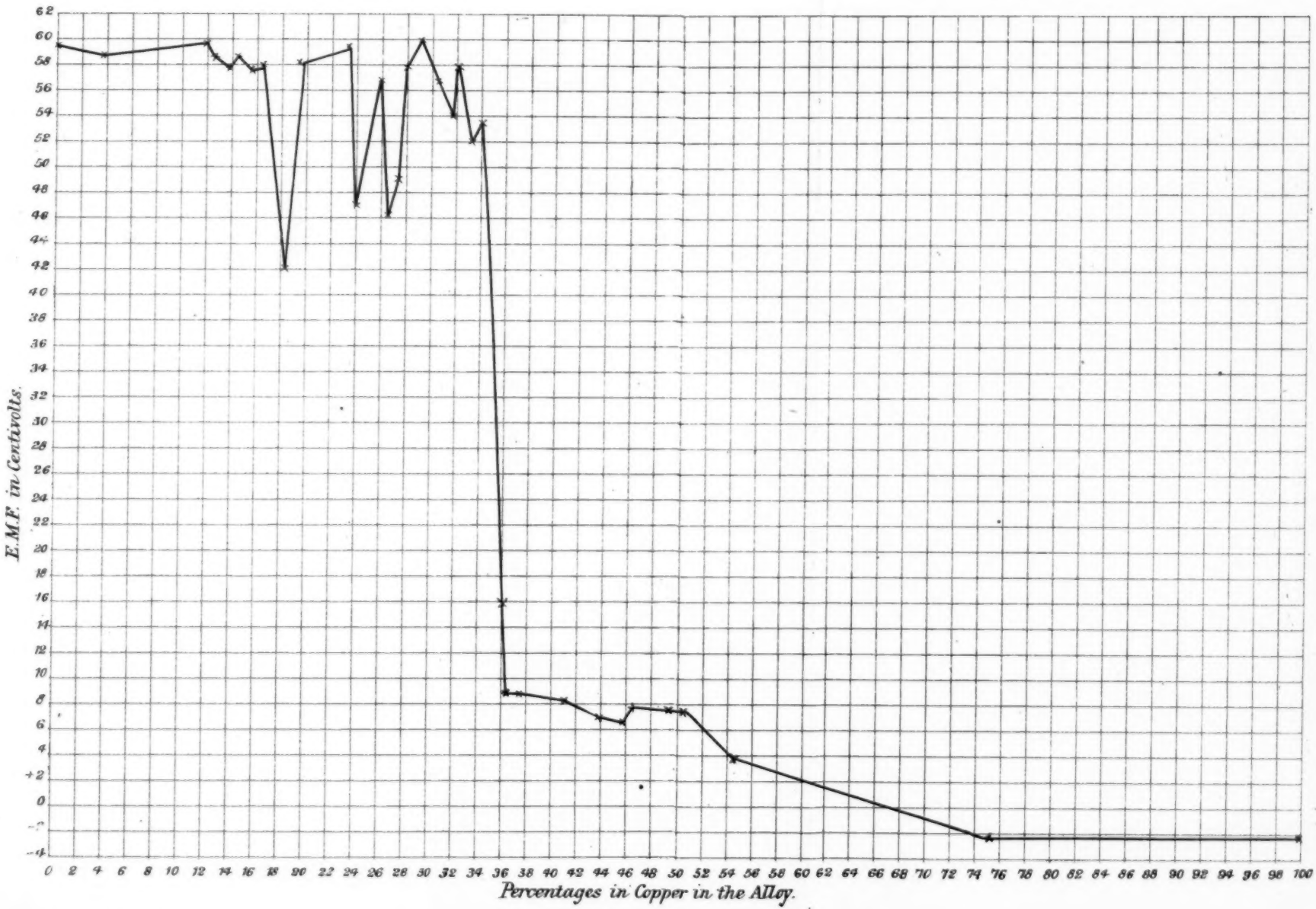
CURVE SHOWING THE ELECTROMOTIVE FORCES OF THE ZINC-COPPER ALLOYS IN THE CUPROUS IODIDE CELL.



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influence may be rendered evident in different cases. At Dr. Armstrong's suggestion, I have therefore investigated the dependence of change in electrical conductivity on composition in the case of sulphuric acid and of a number of other typical solutions, in the hope of throwing further light on this question. The number of excellent determinations given by F. Kohlrausch (*Ann. Phys. Chem.*, 1875, **154**, 215; 1876, **159**, 233; 1879, **6**, 1), and the extension of the numbers for sulphuric acid from H_2SO_4 to $H_2S_2O_7$ by W. Kohlrausch (*ibid.*, 1882, **17**, 69), rendered this a comparatively easy task.

Taking the curves which show the relation between electrical conductivity and percentage composition, one peculiarity will be noticed as common to nearly all: that they rise from zero and after attaining a maximum more or less gradually fall back again to zero. To all appearances, the curve between the two zero points is absolutely continuous. The curve for sulphuric acid differs, however, in a remarkable manner from the rest in having two maxima, the one at a point *intermediate* between the compound H_2SO_4 and the first hydrate, $H_2SO_4 \cdot OH_2$, and the second *beyond* the point where the hexahydrate is situated. It was a question of much interest whether by treating the electrical conductivity as a function of the percentage composition and differentiating in Mendeléeff's manner this curve could not be broken up so as to give evidence of the definite hydrates before mentioned.

This is therefore what has been done, the result being shown in the appended curves. It will be seen at once that the result thus far has been disappointing, inasmuch as the curve obtained by plotting the differential expressing the change of conductivity with percentage composition, $\frac{dk}{dp}$, against the percentage composition does not give the broken curve expected but one which is to all appearance continuous. The form of this curve excluded the idea which I at first entertained that the conductivity might be a parabolic, non-continuous function of the percentage composition.

There was, however, obviously a possibility that the function might be of the third order, and in this case if—

$$K = A + Bp + Cp^2 + Dp^3,$$

we should have—

$$\frac{d^2k}{dp^2} = 2C + 6Dp,$$

that is, the second differential coefficient would, between certain limits, be a rectilinear function of the percentage composition. On taking the second differential coefficient, this was found to actually be the case: it is indeed evident that the resulting curve consists of a series

of rectilinear curves showing breaks, and what is most important that these breaks occur at points corresponding with the composition of the hydrates discovered by Mendeléeff, with the addition of one other, namely, $H_2SO_4 \cdot 24OH_2$.

The numbers by means of which the curves for the conductivity and first and second differential coefficients of sulphuric acid have been drawn are given below. The differential coefficients have been

I. *Sulphuric Acid.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{dk^2}{dp^2}$.
1·03	443	0·51	430	1·14	− 29·3
2·51	1026	1·77	393	2·76	− 13·6
5·02	1944	3·76	366	5·65	− 7·1
10·05	3679	7·55	339	10·12	− 11·1
15·33	5168	12·69	282	15·16	− 16·2
19·95	6100	17·64	202	20·03	− 16·9
24·89	6701	22·42	122	24·91	− 16·2
29·92	6911	27·40	41·7	29·89	− 13·5
34·87	6784	32·39	− 25·6	34·76	− 13·2
39·39	6383	37·13	− 88·5	40·81	− 4·8
49·61	5112	44·50	−124·3	49·64	− 3·1
59·95	3494	54·78	−156·4	59·01	0·6
66·16	2554	63·05	−151·3	65·93	2·3
71·46	1823	68·81	−138·1	71·02	3·5
75·00	1421	73·23	−112·5	75·04	7·8
78·70	1109	76·85	− 84·3	78·61	10·5
82·06	945	80·38	− 48·8	81·82	12·5
84·49	914	83·27	− 12·7	84·40	10·2
86·10	927	85·29	8	86·05	6·7
87·52	954	86·82	18·3	88·21	0·8
90·50	1014	89·01	20·1	90·35	− 5·8
92·90	1025	91·7	4·5	92·87	− 16·1
95·20	948	94·05	− 33·4	95·04	− 48·2
96·87	790	96·03	− 95·4	96·58	− 51·8
98·42	553	67·14	−152·9	97·94	−108·1
99·08	337·4	98·75	−327	99·00	−112
99·44	199·0	99·26	−384		
100·14	175				
100·21	185·6	100·17	151·4	100·23	−492
100·40	202·2	100·30	87·4	100·40	− 2·4
100·63	222·2	100·51	86·9	100·69	− 73·6
101·12	251·8	100·87	60·4	101·04	− 93·2
101·30	257	101·21	28·7	101·45	− 25·2
102·08	270	101·69	16·6	102·24	− 25·5
103·53	253	102·80	− 11·7	103·68	− 13·6
105·61	179	104·57	− 35·6	105·59	− 5·1
107·61	86·8	106·61	− 46·1	107·25	0·6
108·19	60·5	107·90	− 45·3	108·17	21·1
108·70	43·2	108·44	− 33·9	108·69	27·2
109·20	33·2	108·95	− 20	109·21	4·1
109·74	23·6	109·47	− 17·9	109·76	2·5
110·38	13·05	110·06	− 16·5		

calculated by taking the differences between consecutive observations and dividing by the differences of the corresponding percentages; although this does not give true differentials, yet where the observations are accurate the errors thus introduced are small, and this method has the advantage of employing only the actual observed values: so that the curves may be said to be deduced directly from experiment.

This most important concurrence with Mendeléeff's result, besides helping to confirm the latter, proves that the electrical conductivity of sulphuric acid, if not wholly due to, is very largely influenced by, the formation of definite hydrates in solution; and that the rectilinear character of the second differential coefficient curve gives us the means of ascertaining what hydrates there are which exercise this influence. That this is true for other solutions besides that of sulphuric acid has been likewise ascertained, and in each case it has been found that the points where breaks occur on the $\frac{d^2k}{dp^2}$ curve exactly correspond with those which occur on Mendeléeff's curve for the change of density with percentage composition $\frac{ds}{dp}$.

From the form of the second differential coefficient curve, it can easily be seen where breaks in the continuity of the conductivity curve may be expected, and equations of the form $K = A + Bp + Cp^2 + Dp^3$ may be constructed for the various continuous portions of the conductivity curve. Thus the conductivity at 18° of a solution $H_2SO_4mOH_2$ is expressed by means of the following equations:—

From $m = \frac{1}{12}$ to $m = 1$,

$$K = -34396 - 758{\cdot}97p - 3{\cdot}878p^2 - 0{\cdot}00205p^3 \quad . \quad . \quad (1)$$

From $m = 1$ to $m = 2$.

$$K = -860 + 617{\cdot}5p - 13{\cdot}88p^2 + 0{\cdot}0807p^3 \quad . \quad . \quad . \quad . \quad (2)$$

From $m = 2$ to $m = 6$.

$$K = 5321 + 252{\cdot}9p - 7{\cdot}38p^2 + 0{\cdot}044p^3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From $m = 6$ to $m = 24$.

$$K = -1456 + 624{\cdot}58p - 14{\cdot}194p^2 + 0{\cdot}0866p^3 \quad . \quad . \quad . \quad (4)$$

From $m = 24$ to $m = 150$.

$$K = 69{\cdot}3 + 386{\cdot}22p - 1{\cdot}494p^2 - 0{\cdot}1418p^3 \quad . \quad . \quad . \quad . \quad (5)$$

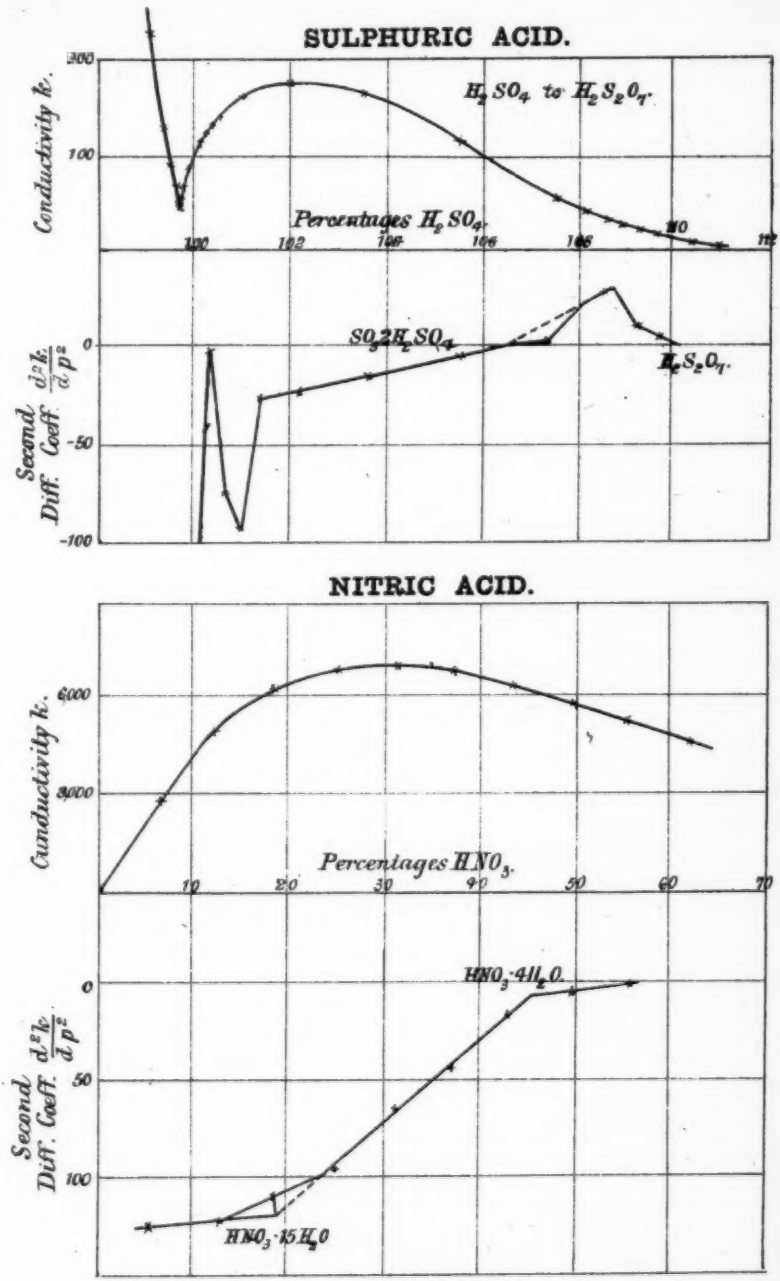
where p is the percentage of acid in the solution. These equations are only applicable strictly between the limits stated. The values deduced by their application agree most satisfactorily with the observed values in the case of (3), but in no case does the average

difference between the calculated and observed values exceed 1 per cent.

Reverting to the sulphuric acid curve, I would call attention to the following points:—The addition to the acid of any quantity of water up to about 2 per cent. does not appear to influence the electrical conductivity in any regular manner, the second differential curve changing its direction in totally irregular fashion. But when the acid is of such a strength that it contains about 98 per cent. H_2SO_4, the conductivity is influenced perfectly regularly by further dilution up to $H_2SO_4 \cdot OH_2$, the second differential curve between these limits being a continuous straight line. It is specially noteworthy that no change takes place in the differential coefficient curve between these points corresponding with the maximum attained by the conductivity curve. The maximum is evidently due to some influence exerted by both the compounds H_2SO_4 and $H_2SO_4 \cdot OH_2$ on the conductivity in such a way that at this point the sum of the influence of each becomes a maximum. It will be noticed that the second maximum on the conductivity curve is also in no way indicated on the second differential curve, but that it lies between the hydrates $H_2SO_4 \cdot 6OH_2$ and $H_2SO_4 \cdot 24OH_2$, and this is to be explained in a similar manner. On passing the last "hydrate" indicated, namely, $H_2SO_4 \cdot 150OH_2$, the second differential curve assumes again a perfectly irregular form just as at the commencement, and this irregularity continues up to the end. This irregularity at each end of the curve is a point of special interest.

If we start again from the compound H_2SO_4 and proceed in the opposite direction towards $H_2S_2O_7$, we find in this case an exact parallel to what formerly happened. Up to a point corresponding with about 102 per cent. H_2SO_4, the second differential coefficient curve is absolutely irregular; it then takes the form of a straight line and proceeds regularly till the composition $2H_2SO_4 \cdot SO_3$ is reached, where a break occurs, and the direction of the curve changes slightly. It still proceeds regularly, however, until the point $H_2S_2O_7$ is very nearly reached; and here again it suddenly becomes irregular. The irregularity, in fact, always occurs, and the same is true for every solution besides that of sulphuric acid that has been examined as yet, when the pure compound begins to undergo dilution. It may be taken as representing an initiative stage during which the action of the compounds that are just beginning to be formed has not come fully into play, and the conductivity varies with a series of physical actions which here probably take place and does not assume that regularity which it afterwards attains when depending solely on the influence of the hydrates formed.

It is on the case of sulphuric acid as offering the greater range,



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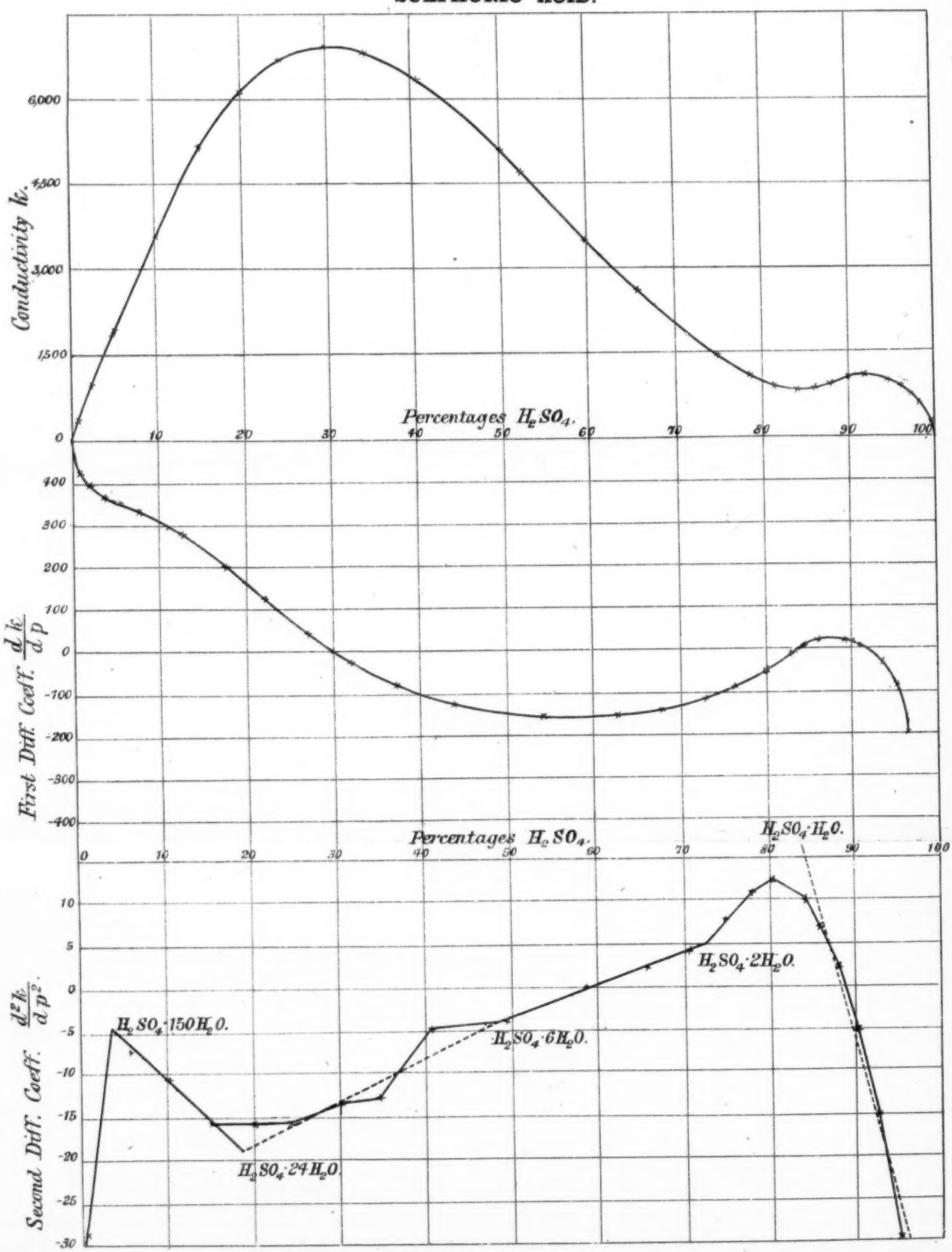
SULPHURIC ACID.



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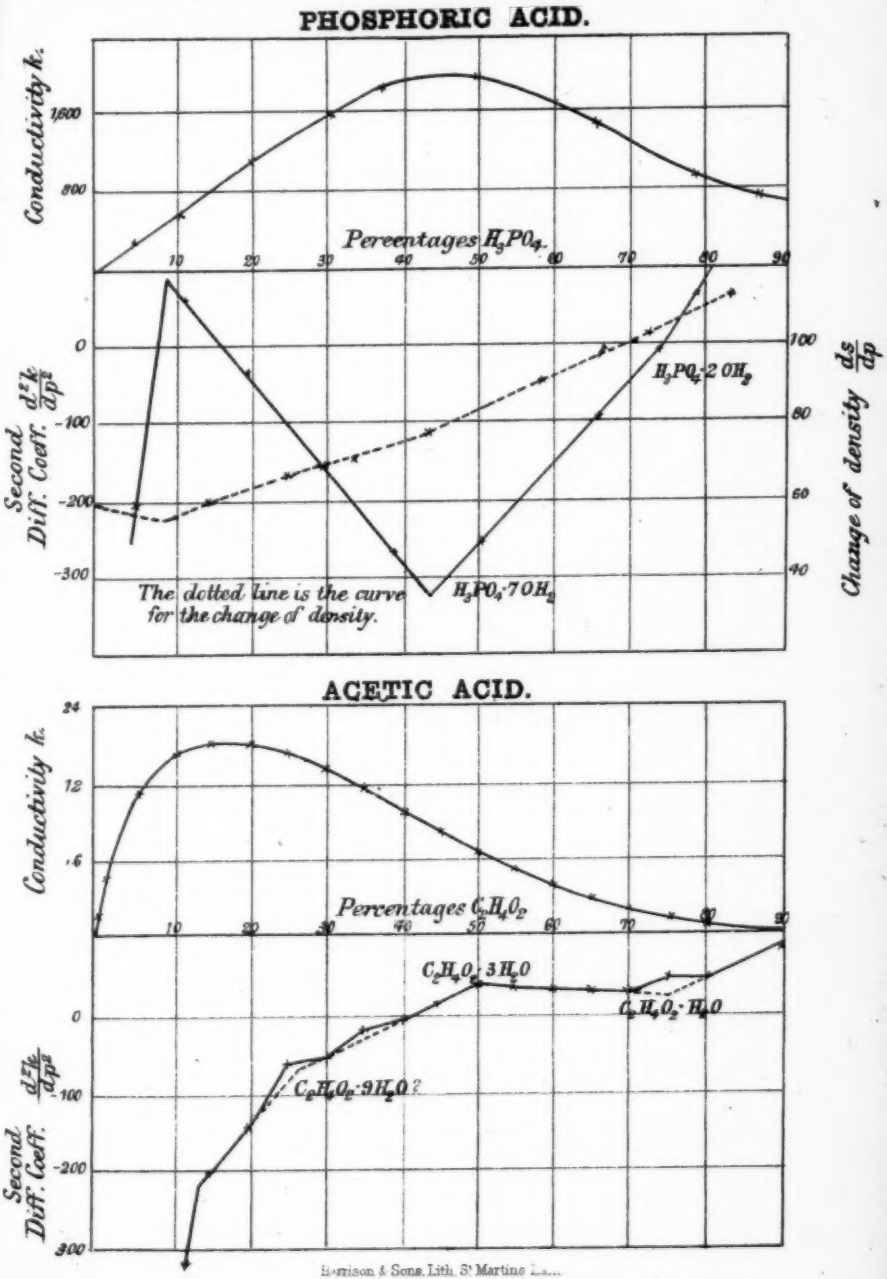

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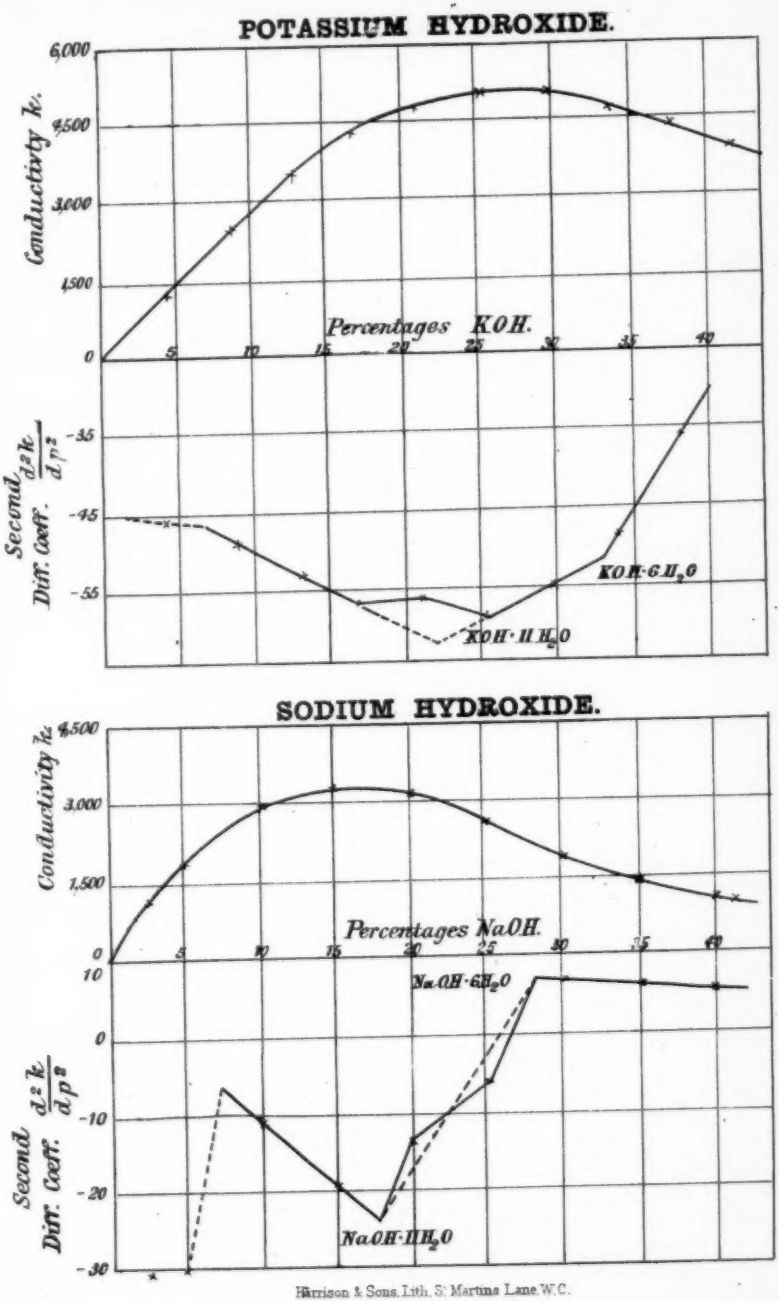

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and the one for which the largest number of determinations have been made, that we may at present rest the hypothesis that electrical conductivity of aqueous solutions is due to the formation and owing to the influence of certain definite hydrates. The sulphuric acid curve is, in fact, typical of all others that have been examined. In the case of nitric acid, for instance, on taking the second differential coefficient there is evidence of the formation of two compounds, $HNO_3 \cdot 15OH_2$ and $HNO_3 \cdot 4OH_2$, and the presence of the same compounds is indicated by Mendeléeff's curve for change of density. It is unfortunate that the numbers for the electrical conductivity do not extend beyond an acid containing 62 per cent. of HNO_3, so that the presence of hydrates richer in nitric acid than the one indicated by $HNO_3 \cdot 4OH_2$ cannot be ascertained.

Phosphoric acid gives a very characteristic curve for the second differential coefficient, and breaks corresponding exactly with those which occur on Mendeléeff's curve occur for the hydrates $H_3PO_4 \cdot 7OH_2$ and $H_3PO_4 \cdot 2OH_2$. In this case also, the observations do not extend far enough to enable it to be ascertained whether a hydrate richer in phosphoric acid exists.

Potassium and sodium hydroxides have likewise been examined, but the numbers in these cases are altogether insufficient for anything like an adequate investigation. It is of interest that in this case the evidence, as far as it goes, tends to prove that potassium and sodium hydroxides form the same hydrates, namely, one with 6 mols. H_2O, and one with 10 to 11 mols.

Acetic acid, a compound with very low conductivity, gives distinct evidence of the formation of two hydrates, $C_2H_4O_2 \cdot OH_2$ and $C_2H_4O_2 \cdot 3OH_2$, and a third hydrate is indicated, most probably having the constitution $C_2H_4O_2 \cdot 9OH_2$.

The following are the numbers from which the curves in each case have been constructed:—

II. *Nitric Acid.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{d^2k}{dp^2}$.
6·2	2924	3·1	−471	6·2	−126
12·4	5072	9·3	345	12·4	−121
18·6	6460	15·5	224	18·6	−107
24·8	7185	21·7	117	24·8	− 95·4
31·0	7319	27·9	21·6	31·0	− 61·4
37·2	7062	34·1	− 39·8	37·2	− 42·8
43·4	6550	40·3	− 82·6	43·4	− 16·6
49·6	5935	46·5	− 99·2	49·6	− 4·8
55·8	5290	52·7	−104	55·8	0
62·0	4646	58·9	−104	62·0	

III. *Phosphoric Acid.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{d^2k}{dp^2}$.
4·92	288	2·46	58·5	5·00	−20·3
10·25	544	7·58	48·1	11·36	6·1
20·05	1061	15·15	52·7	20·23	− 3·6
30·52	1574	25·31	49·0	29·51	−15·5
36·90	1804	33·71	36·0	38·53	−27·3
49·80	1945	43·35	10·9	51·07	−25·3
67·80	1436	58·80	−28·2	66·08	− 9·8
78·93	962	73·36	−42·6	78·18	+ 5·7
87·07	660	83·00	−37·1		

IV. *Acetic Acid.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{d^2k}{dp^2}$.
0·3	2·98	0·15	9·9	0·4	
1·0	5·48	0·65	3·5	1·82	
5	11·47	3	1·467	5·25	−901
10	14·30	7·5	0·5660	10	−390
15	15·18	12·5	0·176	15	−204
20	15·04	17·5	−0·028	20	−132
25	14·24	22·5	−0·160	25	− 64
30	13·12	27·5	−0·224	30	− 56
35	11·72	32·5	−0·280	35	− 22
40	10·13	37·5	−0·318	40	− 10
45	8·49	42·5	−0·328	45	16
50	6·93	47·5	−0·312	50	30
55	5·52	52·5	−0·282	55	34
60	4·28	57·5	−0·248	60	26
65	3·17	62·5	−0·222	65	28
70	2·20	67·5	−0·194	70	28
75	1·37	72·5	−0·166	75	44
80	0·76	77·5	−0·122	83·7	84
99·7	0·0004	90	−0·038		

V. *Potassium Hydroxide.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{d^2k}{dp^2}$.
4·2	1372	2·1	326·6	4·2	−45·6
8·4	2552	6·3	281	8·4	−49
12·6	3526	10·5	232	12·6	−53
16·8	4271	14·7	179	16·8	−57
21·0	4784	18·9	122	21·0	−56
25·2	5061	23·1	66	25·2	−59
29·4	5090	27·3	7	29·4	−55
33·6	4890	31·5	− 48	33·6	−49
37·8	4484	35·7	− 97	37·8	−32
42·0	3944	39·9	−129		

VI. *Sodium Hydroxide.*

p.	K.	p.	$\frac{dk}{dp}$.	p.	$\frac{d^2k}{dp^2}$.
2·5	1019	1·25	407·6		
5	1845	3·75	330·4	2·5	−30·80
10	2927	7·5	216·4	5·62	−30·12
15	3244	12·5	63·4	10	−10·60
20	3062	17·5	− 36·4	15	−19·96
25	2543	22·5	−103·8	20	−13·48
30	1892	27·5	−130·2	25	− 5·28
35	1409	32·5	− 96·6	30	− 6·72
40	1088	37·5	− 64·2	35	− 6·48
42	995	41	− 46·5	39·25	− 5·06

The values for the conductivity which have been used in investigating the above cases are those given by Kohlrausch for the temperature of 18°. It has not been possible, owing to the want of full experimental data, to ascertain what effect change of temperature would have on the second differential curve. According to Mendeléeff's theory, the only effect which a rise or fall of temperature could have on the solution would be to alter the amounts of the products of dissociation, but as the compounds formed would be the same for the same concentrations, no change would take place in the position of the points where breaks occur on the second differential coefficient curve, although the direction of the lines joining those points might be altered. That is, the same hydrates would be formed provided the concentration were kept constant whatever the temperature might be as long as it were short of that which would produce

total decomposition in the hydrates. Proof of this is brought forward by Mendeléeff in his paper on the change of density of sulphuric acid (*loc. cit.*).

This statement as to the effect of temperature is fully verified by the electrical data in the case of nitric acid, the conductivity of which has been determined by Kohlrausch at 0°, 18° and 40°, and working out the second differential from the numbers given for these temperatures, the direction of the straight lines representing the various portions of the second differential curve is found to alter perfectly regularly as the temperature rises or falls, but the breaks occur at the same points for all temperatures.

This being the case, such experiments as those of Heim (*Ann. Phys. Chem.*, **27**, 643) on change of conductivity with change of temperature, and of Nicol (Trans., 1887, 389) on change of specific viscosity with change of temperature, for saturated solutions, cannot be accepted as proving that the composition of saturated and non-saturated solutions is necessarily the same, since where the concentration of the solution undergoes no change the composition must of necessity remain the same. It is only by investigating the change of the physical properties with the concentration that change of composition at the saturation point might be shown to take place, and, as far as can be ascertained from the few experiments quoted by Nicol (*loc. cit.*) on the relation of specific viscosity to concentration, such a change at the saturation point does actually take place. Heim's experiments, on the other hand, may be taken as affording additional support to Mendeléeff's views of the influence of temperature on solutions.

Assuming Mendeléeff's theory to be true, and that what we really have in a solution of two substances at any point is a mixture of two dissociable and dissociating compounds formed from these substances in different proportions, we may deduce an expression for the electrical conductivity of such a solution in the following manner:—

If K is the conductivity of the solution, we may suppose a certain proportion of this to be borne by each constituent of the solution, and if p is the percentage of one constituent, and p_1 the percentage of the other, and a quantity a of the first is combined with a quantity b of the second, the remainders representing the products of dissociation, we have—

$$K = (p - a)k + (p_1 - b)k_1 + (a + b)k_2,$$

where k, k_1 and k_2 are the conductivities of unit amounts of the components present under the conditions of experiment. But it is obvious that the amount a of p which will remain combined will be proportional to the total amount p of the constituent present, all other things remaining constant; and that in like manner the amount b of

p_1 remaining combined, will be proportional to p. Hence the above equation becomes—

$$K = kcp + k_1c_1p_1 + (c_2p + c_3p_1)k_2,$$

where c, c_1, c_2 and c_3 are constants. But now since neither constituent when alone and in a pure condition has any conducting power, it is clear that the conductivity of any one constituent must in some way be influenced by the presence of the others, and I cannot but think that it is not only the simplest but also a fair assumption to make, that this influence will be directly porportional to the amounts of the other constituents present. If this is so, k becomes equal to $100 - p$ multiplied by some constant, and k_1 becomes equal to $100 - p_1$ multiplied by some other constant; or since $100 - p_1 = p$, to p multiplied by a constant. The quantity k_2 in the same way is proportional to p since the amounts combined, c_2p and c_3p, depend on p and p_1 or $100 - p$. But k_2 represents the conductivity of a mixture of two compounds, and the influence of each of the compounds on the other must here also be considered. This influence, as will easily be seen, is likewise porportional to p. Therefore k_2, as representing the conductivity of the combined amounts, becomes proportional to p, and as representing the influence of one compound on the other is also proportional to p; in this way k_2 becomes proportional to p^2. If we now substitute the values for k, k_1 and k_2 in the above equation, and for p_1 write $100 - p$, we should find that it would eventually simplify down to

$$K = Bp + Cp^2 + Dp^3,$$

B, C, and D being constants. The conductivity would thus be represented as a function of the third order of the percentage composition, a relation which, as has been shown, is rendered extremely probable by the nature of the second differential coefficient.

VIII.—*Note on Electrolytic Conduction and on Evidence of a Change in the Constitution of Water; an Addendum to the foregoing Paper.*

By Henry E. Armstrong, F.R.S.

The determination of the nature of electrolytic conduction is of such supreme importance in any discussion of the nature of chemical change and of the laws which determine it,* and the results contained

* Professor Stokes, in his Presidential Address to the Royal Society just delivered, uses the striking words: "So closely is electricity related to chemical

in Mr. Crompton's extension of Mendeléef's conception are, in my opinion, of such a definite and conclusive character, that it appears both permissible and desirable to briefly refer, in the first instance, to current opinions, in order that those who are not specially informed on such matters may gain the necessary clue to understand the questions involved.

In my address to the Chemical Section at the British Association meeting at Aberdeen (Report, 1885), I entered somewhat fully upon the discussion of the subject of *chemical action*, specially directing attention to the absolute interdependence of electrolytic and chemical action, and in order to emphasise the importance of the study of electrolytic phenomena, I quoted the words used the previous year by Lord Rayleigh in his Presidential Address to the Association :—

"From the further study of electrolysis we may expect to gain improved views as to the nature of the chemical reactions and of the forces concerned in bringing them about. . . . . I cannot help thinking that the next great advance, of which we have already some foreshadowing, will come on this side. And if I might without presumption venture a word of recommendation, it would be in favour of a more minute study of the simpler chemical phenomena."

My position at that time is best indicated by the following quotations from my address :—

"The questions 'What is electrolysis? What is an electrolyte?' are all-important to the chemist. . . . . Helmholtz tells us that electrolytes belong to the class of typical compounds, the constituents of which are united by 'atomic affinities,' not to the class of 'molecular aggregates.' Is this the fact? Before chemists can accept this conclusion many difficulties must be removed which appear to surround the question. . . . . The current belief among physicists would appear to be that the dissolved electrolyte—the acid or the salt—is almost exclusively primarily decomposed (Wiedemann, *Elektricität*, 1883, ii, 924). We are commonly told that sulphuric acid is added to water to *make it conduct*, but the chemist desires to know why the solution becomes conducting. It may be that in all cases the 'typical compound' is the actual electrolyte—*i.e.*, the body decomposed by the electric current—*but the action only takes place when the typical compounds are conjoined and form the molecular aggregate*, for it is an undoubted fact that HCl and H_2SO_4 dissolve in water, forming 'hydrates.' This production of an 'electrolytical system' from dielectrics is, I venture to think, *the* important question for chemists to consider. I do not believe that we shall be able to

action, that could we only clearly apprehend the nature of electricity, it seems not unlikely that an unexpected flood of light might be shed on chemical combination."

state the exact conditions under which chemical change will take place until a satisfactory solution has been found.

"F. Kohlrausch (*Pogg. Ann.*, 1876, 159, 233) has shown that, on adding sulphuric acid to water, the electric conductivity increases very rapidly until when about 30 per cent. of acid is present a maximum (6914) is attained; conductivity then diminishes almost as rapidly, and a minimum (913) is reached when the concentration corresponds with that of a monohydrate (H_2SO_4,OH_2); from this point conductivity increases somewhat (to 1031 at 92·1 per cent. H_2SO_4), and then again falls, and is probably zero for the pure acid; on adding sulphuric anhydride to the acid conductivity again increases. Solutions of other acids and of a number of salts—chiefly deliquescent and very soluble salts—also exhibit maximum conductivity at particular degrees of concentration. In no other case has the existence of two maxima, such as are observed in solutions of sulphuric acid, been established; but probably this is because the experiments either have not been, or cannot well be, carried out with pure substances or very concentrated solutions. Solutions of less soluble salts increase in conductivity as the amount of salt dissolved increases.

"Kohlrausch has suggested, as an explanation of the influence of the 'solvent' on the conductivity of an 'electrolyte,' that in a solution the ions which are being transferred electrolytically come less frequently into collision than would be the case in the pure substance. There is therefore less opportunity for the formation of new molecules, and the ions are able to travel farther before entering into combination.

"Regarding the question from a chemist's point of view, however, I cannot help thinking that this explanation is scarcely satisfactory or sufficient; and I cannot resist the feeling that the production of electrolytically conducting solutions from dielectrics is in some manner dependent upon the occurrence of chemical change. If the composition of the solutions of maximum conductivity be calculated, it will be seen that they contain but a limited number of water molecules; thus the solution of sulphuric acid of maximum conductivity (at 18°) contains 30·4 per cent. of acid, and therefore has the composition $H_2SO_4 : 12·4\ H_2O$ (approximately); for nitric acid the ratio is 1 : 8; for acetic acid it is about 1 : 17. Now, it is highly remarkable that the solutions of maximum electric conductivity are also very nearly those in the formation of which nearly the maximum amount of heat is developed; this will at once be obvious on comparison of the curves given by Thomsen (*Thermochemische Untersuchungen*, 3), and by Kohlrausch. In the chemist's experience, the point of maximum heat development is usually near to the point of maximum chemical change, and I think therefore that we are justified in con-

cluding that, even, if electrical conductivity be not a maximum at a particular concentration on account of the presence of a particular hydrate (belonging to the class of molecular aggregates) in maximum amount, at all events the 'structure' of the system is especially favourable, and the 'chemical influence' exerted by the one set of molecules upon the other is at a maximum at the point of maximum conductivity. The fact that the amount of sulphuric acid required to form a solution of maximum conductivity increases with temperature—

Temp.....	0°	10°	20°	30°	40°	50°	60°	70°
Per cent.....	30·2	30·9	31·7	32·5	33·5	34·1	34·5	35·4

and also the fact that the maxima and minima of conductivity tend to become obliterated with rise of temperature (Kohlrausch), are both in accordance with the view that conductivity is in some way dependent upon chemical composition, as the effect of rise of temperature would be to cause the dissociation of hydrates such as I have referred to. The increase in conductivity of aqueous solutions with rise of temperature would appear to be against the view here put forward; but it is probable that this may be largely due to diminution in viscosity and increase in the rate of diffusion."

In March of last year I submitted to the Royal Society a paper "On Electrolytic Conduction in relation to Molecular Composition," &c. (*Proc. Roy. Soc.*, 1886, 268), in which I pointed out that it was perhaps desirable to distinguish between *simple electrolytes*—such as fused silver chloride, and *composite electrolytes*—conducting mixtures of compounds like water, hydrogen chloride, and sulphuric acid, which behave as dielectrics when pure. The difference between simple and composite electrolytes was so great that it was difficult to resist the feeling that the mode in which their electrolysis was effected was different, and I ventured to suggest this, without, however, attaching any particular importance to the point, and rather with the object of inciting debate; but I clearly stated my objections to the current dissociation hypothesis of electrolysis, and formulated the view that in the case of composite electrolytes both constituents were immediately concerned, and that the one, the solvent, did not merely exercise a screening effect, as suggested by Kohlrausch.

Considerable discussion on these points has taken place between Professor Lodge and myself, as co-secretaries of the B. A. Electrolysis Committee, and in a communication to this committee at the recent Manchester meeting, in answer to his criticisms, I stated "the chief reasons which cause me to hesitate in accepting the 'atomic dissociation hypothesis' and which have led me to suggest an alternative 'molecular hypothesis,' viz., that in the case of composite

electrolytes, at all events, electrolysis is the outcome of the combined action of the E.M.F. and of some effect which the one set of molecules exerts upon the other set while both are under the influence of the E.M.F." And I added, "I care little at present what the effect is, the important question to settle being whether electrolysis is primarily an affair of atoms or of molecules. . . . Ostwald's remarkable contributions to our knowledge of molecular conductivity appear to me to bear continuous testimony to the existence of such an influence of molecule upon molecule as that I have pictured" (*Electrician*, August 5th and 26th, 1887).

I venture now to contend that, thanks to our illustrious Russian *confrère*, the "great advance" of which Lord Rayleigh spoke is no longer far distant, and that it is patent that electrolysis is primarily an affair of molecules; that electrolysis takes place in consequence of an influence which one set of molecules, A, exercises upon another set of molecules, B. The results which Mr. Crompton has obtained are to my mind conclusive on this point, the information afforded by the study of sulphuric acid solutions being alone sufficient; and they are of special importance as indicating the superiority of electrical values over all others in any discussion of the constitution of complex systems of dissociable compounds.* This was to be expected, as, on the hypothesis now under discussion, the variations in the electrical values would represent variations in the extent to which the one set of molecules affect the other set, the electrical values serving in fact *to quantify an influence;* for changes in constitution or structure might well occur which would involve but a slight degradation of energy and consequently a slight change in density and many other physical properties, and which yet might lead to a relatively very considerable change in the extent to which the compound could exert an influence on the course of electrolytic or chemical change.

In the case of sulphuric acid the evidence is all but complete, and it is no exaggeration to say that every peculiarity of the acid is faithfully pictured in the second differential coefficient curve.

It is well known that H_2SO_4 readily loses SO_3, and that Marignac's experiments have shown that a stable equilibrium is attained only when the acid has lost anhydride to the extent required to form a hydrate $H_2SO_4 \cdot \frac{1}{12}H_2O = 12H_2SO_4 \cdot H_2O$. A sudden change in the direction of the curve will be seen to occur at a point where this "hydrate" is situate; and if the same interpretation be given of this and of the subsequent inflexions, it would appear necessary to admit the existence of such a hydrate, although it is not usually recognised, it being supposed rather that equilibrium is established between

* It is to be expected that the discussion especially of optical and magneto-optical data will afford valuable results in the case of non-electrolytes.

H_2SO_4, $H_2SO_4{\cdot}OH_2$, &c., when the composition is that of Marignac's hydrate. I shall again refer to this point later on, and will only add that Mendeléeff's curve does not show this hydrate.

The three hydrates $H_2SO_4{\cdot}OH_2$, $H_2SO_4{\cdot}2OH_2$, $H_2SO_4{\cdot}6OH_2$ are indicated both on the conductivity curve and on Mendeléeff's density curve, and there is also a marked break on both curves approximately at a point corresponding to a hydrate, $H_2SO_4{\cdot}150H_2O$. The conductivity curve, however, affords an unmistakable indication of a hydrate $H_2SO_4{\cdot}240H_2$, which does not occur on the density curve. The discovery of this hydrate is of fundamental importance, owing to the fact that the maximum conductivity of sulphuric acid solutions is manifested between the points where the two hydrates $H_2SO_4{\cdot}6H_2O$ and $H_2SO_4{\cdot}24H_2O$ are situate: the two sets of molecules which mutually affect each other and induce electrolysis thus become exhibited.

Mr. Crompton's curve shows an inflexion at a point corresponding to the compound $2H_2SO_4{\cdot}SO_3$. I am not aware that any such substance is known, or that salts of such an acid have been described, but a trichromate of somewhat analogous composition has been obtained, and Weber has prepared octosulphates, $M_2SO_4{\cdot}8SO_3$. On writing to my friend Dr. Messel, who is accustomed to observe the behaviour of sulphuric anhydride on the large scale, I learnt "that mixtures of the acid and anhydride containing up to 29—30 per cent. of the latter are liquid at ordinary temperatures, but that then crystallisation takes place; when more than 55 per cent. of anhydride is present, liquids are again obtained, but solidification takes place when a little more than 70 per cent. of anhydride is present." Now—

$2H_2SO_4 \cdot SO_3$,	contains	28·9	per cent.	SO_3.
$2H_2SO_4{\cdot}2SO_3$,	„	41·6	„	„
$2H_2SO_4{\cdot}3SO_3$,	„	55·0	„	„
$H_2SO_4{\cdot}3SO_3$,	„	71·0	„	„

There is, therefore, independent evidence of the existence of the compound indicated on the conductivity curve, and there can be little doubt that other similar compounds will be proved to exist when search is made for them.

The concurrence of the evidence derived from the mathematical discussion of data deduced by the observation of properties so different as density and electric conductivity with what may be termed the chemical evidence afforded by the recognition of a variety of distinct compounds of sulphuric acid with its anhydride or with water is so complete, that I feel we need have no hesitation in applying Mendeléeff's method and in accepting the conclusions to which

it logically leads, even when these are beyond control by any ordinary chemical method.

There is reason to believe that not only water and sulphuric acid, but liquids generally, consist of complexes of the fundamental molecules; and in any discussion of electrolytic conduction it is of primary importance to recognise that this is probably the case. Mendeléeff is prepared to admit the existence of a hydrate containing $150OH_2$, but I must confess that I hesitate to do so, and I even think that the inflexion in the curve at the point corresponding to this supposed hydrate is evidence of a change in the constitution of water. The occurrence of a similar change in the curve at about the same point in the case of ammonia and acetic acid, and at a point somewhat more distant from its origin in the case of phosphoric acid, affords confirmation of this view. It is possible also to put the same interpretation upon the sudden inflexion of the curve at the point corresponding to Marignac's hydrate. Any difficulty which might be felt in admitting the existence of hydrates so abnormal in composition as $12H_2SO_4 \cdot OH_2$ and $H_2SO_4 \cdot 150H_2O$ would then be removed. But it is also conceivable that Marignac's hydrate has an existence, and that it is a hydrate of a polymer of sulphuric acid—not of the fundamental molecule H_2SO_4—consisting of a very limited number of complexes of H_2SO_4 molecules associated with a single water molecule.

The assumption that sulphuric acid mainly consists of complexes such as may be represented by the formula $(H_2SO_4)_x$ would serve to explain many features of the conductivity curve near to its origin from the acid: thus, the low conductivity of concentrated solutions may be attributed to the presence chiefly of $(H_2SO_4)_x$ molecules and of hydrates derived therefrom; and it may be supposed that as the complexes become more and more resolved into hydrates of the fundamental molecule H_2SO_4 by dilution a greater influence would be exercised by molecule upon molecule.

A somewhat similar view to that here indicated has been advanced by Landolt (*Optischedrehungsvermögen*, p. 59), in explanation of the influence of "neutral" solvents on the rotatory power of optically active substances such as turpentine.* But the chief evidence in favour of such an explanation is probably to be found in the influence

* Mr. Crompton has discussed among others the values given by Landolt as representing the change in rotatory power on diluting nicotine with water and turpentine with benzene and acetic acid: the curves afford the clearest indications of the presence of molecular compounds of the active substance with the solvent, but the determinations are not nearly numerous enough to permit of the discovery of the composition of these compounds. I therefore propose to reinvestigate the behaviour of turpentine.

which a small quantity of one metal—for instance, lead or bismuth—exercises on another—for example, on gold—the most ductile of metals, a minute percentage rendering it highly brittle. It is inconceivable that the lead can enter into uniform relationship with the gold molecules throughout the mass, *i.e.*, that it can combine with the whole of them. In the pure gold the molecules are probably throughout uniformly and continuously related, and very probably also they are of simple atomic constitution but not truly symmetrical: on the introduction of a small proportion of foreign incompatible molecules continuity becomes disturbed; the atoms become free to re-arrange themselves, and in place of the uniform relationship which previously obtained a non-uniform relationship results in consequence of the formation of complex aggregates which have less power of cohering than the original simpler molecules. It is, perhaps, an argument in favour of this "screen" hypothesis that, as already pointed out, the marked change in the curve near to the origin from water takes place in the case of phosphoric acid later than in the case of sulphuric: it is not improbable that the molecules of the former acid are of greater complexity than those of the latter, so that if a certain proportion of foreign molecules be necessary to produce maximum effect a larger absolute proportion of phosphoric acid would be required. Considerations of this character, whatever their value in the present instance, are certainly of importance in connection with the study of the influence of small quantities of foreign substances on the properties of metals generally, and in preventing superheating, superfusion, &c.

If the argument advanced in this and the foregoing paper be correct, it becomes more than ever necessary to consider the grounds on which the conclusion is based that electrolysis is the outcome of atomic dissociation. It has always appeared to me that Kohlrausch's curve for sulphuric acid affords the most positive evidence that electrolysis cannot be a simple dissociation phenomenon, as in that case it is to be expected that dissociation would take place to a gradually increasing extent until a maximum was reached and not as the curve would indicate, that after attaining a maximum it should diminish and then again increase until a much higher maximum is attained. The first differential curve may be regarded as picturing the manner in which the influence is exercised at various points by the compounds whose existence is indicated on the second differential curve: and this curve most clearly indicates that the effect is exerted mainly at two points—the one lying between the acid and the bihydrate, and the other between the two hydrates containing 6 and $24OH_2$: the discontinuity of the phenomena at points intermediate between these two principal points is very striking. An explanation of the discon-

tinuity has already been given, viz., that it is due to the fact that in the one case the polymerised acid, in the other the fundamental molecule is active; and if it be difficult to understand the changes which occur on passing from acid to water on the dissociation hypothesis, it is undoubtedly still more difficult to understand the sudden rise and subsequent fall in conductivity on passing from sulphuric to pyrosulphuric acid, and to account for the fact that the latter has a lower conductivity even than the former acid. On my hypothesis, however, the fact that $H_2S_2O_7$ is chemically in a certain sense the more stable compound affords a sufficient explanation of the difference in its behaviour and that of sulphuric acid.

Any conclusion relating to electrolytic phenomena will doubtless be found to apply equally to allied chemical phenomena: so that if it be asserted that too much stress has been laid on the part which atomic dissociation plays in electrolysis, the same remark must be made regarding its influence on the course of chemical change. Certainly, the more I study the subject experimentally, the more the conviction is forced on my mind that an explanation of the majority of chemical changes will ultimately be found in the principle of *association*, and not in that of *dissociation*.

Reference was made in the early part of the paper to the division of electrolytes into two classes of simple and composite electrolytes. There is no reason to cease making this distinction: on the contrary. But it being established, as I believe, that in the case of solutions electrolysis is the outcome of the influence exerted on each other by molecular aggregates consisting of the same proximate elements but differently constituted, there appears no longer to be any necessity to suppose that there is any fundamental difference in the mode in which electrolysis takes place in solutions and in fused salts, *i.e.*, simple electrolytes. It is in the highest degree probable that fused salts contain molecules of different orders of complexity, and it may fairly be supposed that these would be capable of influencing each other much in the same way that I suppose the different aggregates in aqueous solutions influence each other.

With regard to the nature of the influence thus pictured as exerted between molecule and molecule, I do not propose to discuss this now, and would only add that my views are entirely based on the assumption of the existence of what I have termed "residual affinity," and that they necessarily involve the recognition of the potency of this factor.

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IX.—*On the Alleged Existence of a Second Nitroethane.*

By Wyndham R. Dunstan, Professor of Chemistry to the Pharmaceutical Society, and T. S. Dymond.

In 1873, Victor Meyer (*Annalen*, **171**, 1—56) found that by the interaction of ethyl iodide and silver nitrite two compounds of the formula $C_2H_5NO_2$ were produced. One of these he recognised as the previously known ethyl nitrite (b. p. 16·5°), the other as a new substance (b. p. 113°), to which he gave the name of nitroethane. In this interaction much heat is evolved, and the temperature soon rises far above the boiling point of ethyl nitrite. In order to complete the change, the mixture is heated for some hours with a reflux condenser on a water-bath, when the greater part of the ethyl nitrite will escape unless special means are adopted to condense it; some, however, remains dissolved in the nitroethane, generally with a little ethyl iodide, and on fractionating the liquid a mixture of these three substances will distil below 100°. According to Meyer, the two isomerides are formed in equal quantities.

More recently the interaction of ethyl iodide and dry silver nitrite has been studied, under somewhat different conditions, by Kissel* (*Journ. Russ. Chem. Soc.*, 1882, 226—230; and 1884, 135—140); he adds dry silver nitrite, in small quantities at a time, to the ethyl iodide cooled to 0°, until no further action ensues. The mixture is kept cool and shaken during one day, great care being taken to avoid any permanent rise in temperature. Under these conditions, according to Kissel, no ethyl nitrite is formed, but when the mixture is distilled, a considerable quantity of liquid comes over between 29° and 30°. This fraction is redistilled between 28° and 35°, washed with water, a solution of silver nitrate, and a weak sodium carbonate solution; it is then heated with silver nitrate, and distilled from dry calcium nitrate. The liquid, it is stated, now boils constantly at 29—30°, and on combustion yields results agreeing with the formula $C_2H_5NO_2$. This substance is said to resemble in its properties both ethyl nitrite and nitroethane, but is characterised by its chemical reactions as a nitro-compound. It yields a crystalline sodium-derivative, is violently acted on by hydrochloric acid with the production of a new compound, and forms with solution of ferric chloride a blood-red colour, with solution of copper sulphate a clear

* Kissel's papers have been consulted in the original, and I must take this opportunity to thank my friend Sir Nicholas Elphinstone, to whom I am greatly indebted for a translation from the Russian.—W. R. D.

green, and with a solution of silver nitrate a light-yellow turbidity. As regards the nitroethane proper (b. p. 113°), of which, according to Meyer, half the total amount of liquid consists, Kissel alleges that a yield of from 54 to 66 per cent. may be obtained by adopting the process he has described, the remainder of the liquid being the new isomeride. Kissel also claims to have obtained a corresponding compound (b. p. 43—44°) by the interaction of isopropyl iodide and silver nitrite.

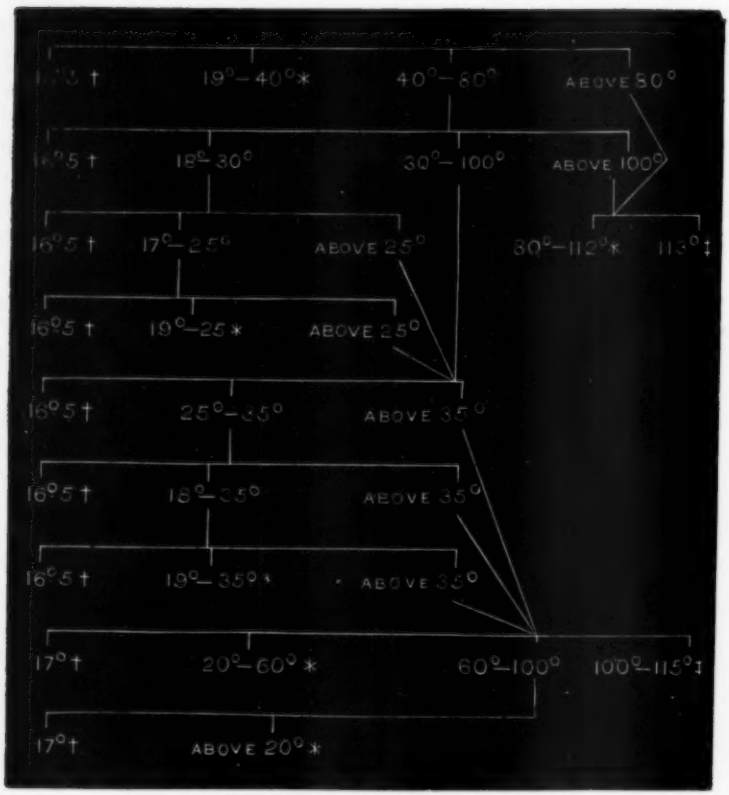
Kissel's description of the properties and reactions of the "second nitroethane" at once suggests the idea that it is merely a mixture of ethyl nitrite with nitroethane, although it is true that some of the alleged facts are inconsistent with this view. We have lately had occasion to prepare a comparatively large quantity of nitroethane, and we thought it worth while to repeat Kissel's experiments.

Dry silver nitrite was gradually added to 180 grams of ethyl iodide cooled below 0°, until there was no further evolution of heat, the mixture was then frequently agitated at a low temperature during one day. No gas escaped. The distillation flask containing the mixture was connected with a condenser, and the temperature slowly raised. Between 16° and 17° a gas was evolved which possessed all the properties of ethyl nitrite. It burned with a yellowish flame, was absorbed by alcohol, and at once liberated iodine from an acid solution of potassium iodide, nitric oxide being set free. The apparatus was now connected with two bulb-condensers, and these were joined to two wash-bottles containing alcohol. Between 19° and 40° a small quantity of liquid condensed; it was tested for ethyl nitrite and nitroethane, both of which were found; the nitroethane was detected by first destroying the ethyl nitrite with excess of an acid solution of ferrous sulphate, and then rendering the liquid alkaline with potash. The alliaceous odour which we had previously observed (*Chem. News*, **56**, 132) whenever nitroethane is reduced with ferrous hydroxide was quite distinct, and by distilling the liquid into diluted hydrochloric acid, and evaporating the distillate to dryness, the hydrochloride of a base was obtained. This was extracted with absolute alcohol and the alcoholic liquid precipitated with ether to remove ammonium chloride, after which the platinochloride was produced in the usual manner and analysed; it contained 39·2 per cent. of platinum, and was thus proved to be ethylamine platinochloride.

Between 40° and 80°, a considerable quantity of liquid distilled; the greater part was condensed in the first bulb, a little, however, was found in the second bulb, and this boiled at 17—18°, consisting almost entirely of ethyl nitrite. Above 80° more liquid distilled and was separately collected. The fraction obtained between 40° and 80° was redistilled; at 16—17° ethyl nitrite passed over,

between 18° and 30° the greater part distilled, a third fraction was collected between 30° and 100°, and a fourth above 100°. From the subjoined table of results, arranged for convenience in the form of a tree, it will be seen that each of these fractions when redistilled is resolved into liquids boiling at a lower and a higher temperature, and by repeatedly fractionating these liquids ethyl nitrite is obtained boiling at 16·5° and nitroethane boiling at 113°. When the fraction was too small to be redistilled, it was tested for ethyl nitrite and for nitroethane, both of which were invariably found. It was often difficult to ascertain exactly the temperature at which distillation commenced,

Table showing the Results of the Fractional Distillation of the Liquid produced by the Interaction at 0°, of Ethyl Iodide and Silver Nitrite.



* Contained both ethyl nitrite and nitroethane.
† Ethyl nitrite.
‡ Nitroethane.

and when two figures are given in the table the first is to be regarded as approximate only. We could discover no liquid which boiled constantly at 29° and 30°; the fraction obtained at this temperature behaved both physically and chemically as a solution of ethyl nitrite in nitroethane. The alcohol in the wash-bottles attached to the bulb-condensers was renewed after each distillation, and when tested, every specimen contained more or less ethyl nitrite which had escaped condensation. It was also noticed that when the original mixture was distilled some nitric oxide escaped, and later distillates contained a little acetic acid.

We are justified in concluding from these results that the so-called "second nitroethane" is indistinguishable from a mixture, or solution, of the two known isomerides of the formula $C_2H_5NO_2$.

X.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XI.—*Bismuth Iodide and Bismuth Fluoride.*

By B. S. Gott, B.A., Scholar of Gonville and Caius College, and M. M. Pattison Muir, M.A.

Bismuth Iodide.

It is known that bismuth iodide, BiI_3, may be prepared either by heating together bismuth and iodine in the ratio Bi : 3I, or by adding an aqueous solution of potassium iodide to a solution of bismuth nitrate in dilute nitric acid. The directions given by earlier experimenters for preparing this compound in the wet way are vague. We have recently made some experiments on the preparation of bismuth iodide, and also on the comparative stabilities towards water of this compound, according as the specimen is prepared in the dry or the wet way.

Preparation of Bismuth Iodide in the Wet Way.—Excess of a fairly concentrated aqueous solution of potassium iodide is added to bismuth nitrate dissolved in the smallest possible quantity of dilute nitric acid; BiI_3 is thus precipitated along with iodine. The precipitate is dissolved in as small a quantity as possible of concentrated aqueous hydriodic acid, and water is added until the greater part but not the whole of the bismuth is precipitated as brown BiI_3. The solid matter

is collected and dried for some time at 100°, whereby most of the free iodine is volatilised. The residue is then washed once or twice with absolute alcohol, and finally dried at 100°.

Some Properties of Bismuth Iodide.—The salt prepared as described above is somewhat soluble in absolute alcohol; 100 parts by weight of alcohol at 20° dissolve about $3\frac{1}{2}$ parts of the salt.

The sp. gr. of BiI_3 prepared in the dry way was found to be 5·64 at $\frac{20°}{20°}$; and the sp. gr. of BiI_3 prepared in the wet way was found to be 5·65 at $\frac{20°}{20°}$.

Specimens of the iodide prepared in both ways were treated with water in about the ratio $BiI_3 : 3000H_2O$, for different times and at different temperatures; the amount of decomposition to BiOI and HI was determined by measuring the quantity of hydriodic acid produced at the expiration of fixed times. The results were as follows:—

	BiI_3 prepared in the dry way.	BiI_3 prepared in the wet way.
Temperature = 26°—		
After 30 minutes' action....	17·5 p. c. decomposed	17·7 p. c. decomposed
„ 60 „ „	19·8 „	19·2 „
„ 150 „ „	24·4 „	23·9 „
Temperature 60—65°.		
After 30 minutes' action....	22·5 „	20·1 „
„ 60 „ „	25·4 „	25·1 „
„ 150 „ „	30·7 „	33·9 „
Temperature = 100°.		
After 30 minutes' action....	22·75 „	23·6 „
„ 60 „ „	27·4 „	29·9 „
„ 150 „ „	35·1 „	35·4 „

There is therefore no appreciable difference between the rate of decomposition by water of the two specimens of bismuth iodide.

Bismuth Fluoride, BiF_3 (comp. Pattison Muir, Hoffmeister, and Robbs, Trans., 1881, **39**, 33).

Preparation.—(1.) Moist freshly precipitated Bi_2O_3,xH_2O is added little by little to hot hydrofluoric acid in a platinum dish, so long as the oxide dissolves fairly easily; the liquid is evaporated to dryness at 100°, and the residue is heated to bright redness in a closed platinum crucible. If the addition of bismuthous oxide to hydrofluoric acid is continued until some remains undissolved, or if the solution of the oxide in the acid is boiled for some time, a considerable

quantity of a double compound of bismuthyl fluoride and hydrofluoric acid, BiOF,2HF, is produced:—

$$Bi_2O_3 + 6HF = 2(BiOF,2HF) + H_2O.$$

(2.) A fairly concentrated aqueous solution of potassium fluoride is added to bismuth nitrate dissolved in the minimum quantity of dilute nitric acid, until the whole of the bismuth is precipitated. The precipitate is washed repeatedly with cold water, and is then suspended in boiling water, which is changed from time to time, until no trace of potassium salt is to be found in the washings. This salt, after drying at 100°, is pure bismuth fluoride, BiF_3.

Bismuth fluoride is a heavy crystalline compound, sp. gr. $\frac{20°}{20°}$ = 5·32. It is unchanged on heating to fusion (about a full red heat). The salt is insoluble in water or alcohol; it does not react with sulphur when the two are heated together; it is not changed by heating in the mixture of nitrogen oxides produced by warming starch with nitric acid. Bismuth fluoride is the most stable of all bismuth haloid compounds.

Preparation of Bismuthyl Fluoride, BiOF.

Moist freshly precipitated Bi_2O_3,xH_2O is added to hot hydrofluoric acid until all acid reaction has disappeared. The solid thus produced is washed with hot water, dried at 100°, and afterwards heated to moderate redness in a closed platinum dish; or the solid is suspended in boiling water, which is changed from time to time until the washings are perfectly neutral to litmus, and the residue is then dried at 100°.

Bismuthyl fluoride is a heavy, white, crystalline powder; sp. gr. $\frac{20°}{20°}$ = 7·5, whether prepared by removing all HF by long continued washing or by heating. It is not changed by heating to moderate redness, but if the temperature is raised to bright redness decomposition occurs. We are now engaged with an examination of the double compounds formed by the union of bismuth haloid salts with the haloid salts of the alkali metals; the results we hope will throw some light on the questions suggested by the term *molecular compounds*.

XI.—*Halogen substituted Derivatives of Benzalmalonic Acid.*

By Charles M. Stuart, M.A., Fellow of St. John's College, Cambridge.

In a previous paper (Trans., 1886, 357), I showed that the presence of a nitro-group in the ortho-position prevented the decomposition of benzalmalonic acid when it was boiled with water; I have now introduced other negative elements into the ortho-position in place of NO_2, and measured the amount of decomposition under the same circumstances.

In preparing these compounds, it was necessary to employ ortho-chloro-, bromo-, and iodo-benzaldehydes; the first of these was obtained by Henry (*Ber.*, **2**, 135) by acting on salicylaldehyde with pentachloride of phosphorus in two successive stages; I found, however, that the reaction is more complicated than he describes, and therefore, deemed it advisable to adopt another method. Starting from ortho-nitrocinnamic acid, we can prepare ortho-chloro-, bromo-, or iodo-benzaldehyde in two ways:—

1. By converting the nitrocinnamic acid successively into the amido- and diazo-derivatives, from which chloro-, bromo- or iodo-cinnamic acids can be prepared. These are then oxidised with permanganate, as described by Einhorn (*Ber.*, **17**, 119).

2. By reducing orthonitrobenzaldehyde to ortho-amidobenzaldehyde, dissolving this in concentrated hydrochloric acid, and adding a solution of sodium or potassium nitrite till the deep red liquid is decolorised, taking care to keep the mixture cool; this solution, containing the diazo-derivative, is then decomposed by a hot solution of cuprous chloride in hydrochloric acid, and the product distilled with steam, when the substituted benzaldehyde is readily obtained.

I found the former of these two processes more convenient for preparing the chloro- and iodo-derivative, and the latter for the bromo-derivative.

Orthochlorobenzaldehyde boils at 210° as stated by Henry.

Orthobromobenzaldehyde melts at 21—22°, and boils at about 230°. The following results were obtained on analysis:—

0·5195 gram substance takes 27·9 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 42·97 Br. Theory .. 43·24

Orthiodobenzaldehyde melts at 37°. On analysis the following result was obtained:—

0·3431 gram substance takes 13·7 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 54·53 I. Theory .. 54·74

A mixture of equal weights of orthochlorobenzaldehyde and malonic acid is heated at 100° for some hours with about half their weight of glacial acetic acid; the crystalline deposit is then collected and washed with glacial acetic acid, water, and chloroform. It melts at 192° with effervescence, leaving a residue which melts again at 196° (orthochlorocinnamic acid). On analysis—

0·3446 gram substance gave 0·6665 gram CO_2 and 0·0984 gram H_2O.

	Found.	Theory. $C_{10}H_7ClO_4$.
C	52·74	52·98
H	3·17	3·09

It is therefore orthochlorobenzalmalonic acid. Its solution neutralised with ammonia gives a precipitate with barium chloride, but not with calcium chloride.

In order to determine the amount of decomposition with water, it was treated as described in my former paper (Trans., 1886, 357).

	KHO sol.	CO_2.
Boiled for one hour.	I. 23·7 c.c.	0·0370 gram.
	II. 23·4 „	0·0425 „
Boiled for 15 minutes.	I. 11·2 „	0·0148 „
	II. 11·2 „	0·0153 „

Orthobromobenzalmalonic acid was prepared by an exactly similar method. It melts at 198° with effervescence, the residue melting again at 208° (orthobromocinnamic acid). Its solution in ammonia yields a precipitate both with barium chloride and calcium chloride. On analysis—

0·4857 gram substance required 17·72 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 29·18 per cent. Br. Theory .. 29·52

2·71 gram with 150 c.c. water—

	KHO sol.	CO_2.
Boiled for one hour.	I. 24·0 c.c.	0·0467 gram.
	II. 24·6 „	0·0450 „
Boiled for 15 minutes.	I. 12·00 „	0·0142 „
	II. 11·76 „	0·0125 „

Orthiodobenzalmalonic acid was obtained in a precisely similar way from orthiodobenzaldehyde. It melts at 204° with effervescence, the residue melting again at about 207° C. (orthiodocinnamic acid). Its solution in ammonia precipitates barium but not calcium chloride.

0·3408 gram substance gave 0·4723 gram CO_2 and 0·0661 gram H_2O.

	Found.	Theory.
C	37·83	37·64
H	2·15	2·20

3·18 gram with 150 c.c. water—

	KHO sol.	CO_2.
Boiled for one hour.	I. 24·6 c.c.	0·0400 gram.
	II. 23·9 „	0·0444 „
Boiled for 15 minutes.	I. 12·0 „	0·0154 „
	II. 11·6 „	0·0132 „

Orthomethoxybenzalmalonic acid was prepared in a similar manner from orthomethoxybenzaldehyde. It melts at 178° with effervescence. Its solution in ammonia precipitates barium but not calcium salts. On analysis—

0·3621 gram substance gave 0·7851 gram CO and 0·1239 gram H_2O.

	Found.	Theory.
C	59·13	59·45
H	3·80	4·50

2·22 gram boiled with 150 c.c. water—

	KHO sol.	CO_2.
Boiled for one hour.	I. 28·4 c.c.	0·0359 gram.
	II. 27·8 „	0·0408 „
Boiled for 15 minutes.	I. 16·75 „	0·0120 „
	II. 16·00 „	0·0090 „

All these numbers together give us the following table of decompositions, the equations being—

I. $C_6H_5{\cdot}CH : C(COOH)_2 + H_2O = C_6H_5{\cdot}COH + CH_2(COOH)_2$,

II. $C_6H_5{\cdot}CH : C(COOH)_2 = C_6H_5{\cdot}CH : CH{\cdot}COOH + CO_2$,

benzalmalonic acid and its orthonitro-derivative being introduced from my previous paper for the sake of comparison.

	Boiled for 1 hour. Decomposition according to			Boiled for 15 minutes. Decomposition according to		
	Eq. I.	Eq. II.	Total.	Eq. I.	Eq. II.	Total.
Benzalmalonic acid.....	85·8	10·8	96·6	57·8	1·41	59·2
	84·4	10·6	95·0	58·3	1·25	59·5
Orthonitrobenzalmalonic acid.	24·5	5·7	30·2	8·70	1·18	9·88
	23·6	6·5	30·1	8·71	1·25	9·96
	24·4	6·4	30·8	—	—	—
Orthochlorobenzalmalonic acid	65·17	8·40	73·57	30·8	3·36	34·16
	64·35	9·64	73·99	30·8	3·47	34·27
Orthobromobenzalmalonic acid	66·0	10·6	76·6	33·0	3·22	36·22
	67·6	10·2	77·8	32·3	2·84	35·14
Orthiodobenzalmalonic acid ..	67·6	9·09	76·69	33·0	3·5	36·5
	65·7	10·09	75·79	31·9	3·0	34·9
Orthomethoxybenzalmalonic acid	78·1	8·16	86·2	45·9	2·72	48·62
	76·4	9·27	85·6	44·0	2·04	46·04

This table shows that the halogens in the ortho-position have a certain protecting influence on the hydrocarbon side-chain, but considerably less than that of the group NO_2; the protecting power of chlorine is slightly greater than that of bromine or iodine, the two latter having apparently the same influence. Slight differences here are possibly owing to the greater or less volatility of the aldehyde in steam.

The protecting influence of the group MeO is less than that of any of the halogens.

It will be interesting to see what is the influence of fluorine in the ortho-position, and on this I am at present employed.

Reduction of Orthonitrobenzalmalonic Acid.

An ammoniacal solution of orthonitrobenzalmalonic acid was added to a hot solution of 10 times its weight of crystallised ferrous sulphate saturated with ammonia; on acidifying the filtered solution, a precipitate was obtained which was insoluble in water, ether, and alcohol, but which crystallised from glacial acetic acid in small golden needles. On analysis —

0·3368 gram substance gave 0·7835 gram CO_2 and 0·1072 gram H_2O.

	Found.	Theory. $C_{10}H_7NO_3$.
C.....	63·44	63·49
H.....	3·53	3·70

It is therefore carbostyrilcarboxylic acid, and is identical with the compound which Friedlander and Göhring obtained by the condensation of orthamidobenzaldehyde with malonic acid (*Ber.*, **17**, 459). It melts above 320°, and bears the same relation to coumarincarboxylic acid that carbostyril does to coumarin. Friedlander and Göhring represent its formula as $C_6H_4\begin{cases}N{=}C\cdot OH\\ CH:C\cdot COOH\end{cases}$, but it is difficult to see how a substance of this composition could be formed by the reduction of orthonitrobenzalmalonic acid. It appears to me that the formula $C_6H_4\begin{cases}NH\cdot CO\\ CH:C\cdot COOH\end{cases}$, is more probable.

XII.—*Action of Hydrogen Sulphide on Arsenic Acid.*

By Bohuslav Brauner, Ph.D., F.C.S., late Berkeley Fellow of Owens College, and F. Tomíček.*

(Communication from the Chemical Laboratory of the Bohemian University, Prague.)

The treatment of solutions of arsenic acid, or acid solutions of arsenates with hydrogen sulphide, is an operation which is carried out daily in chemical laboratories, but there is a difference of opinion as to the reactions which take place under these circumstances.

Historical Introduction.

According to Berzelius (*Ann. Phys. Chem.*, 1826, **7**, 2) arsenic pentasulphide is formed when hydrogen sulphide acts on a moderately concentrated solution of arsenic acid. Gmelin (*Handb.*, **5**, ed. ii, 690 [1853]) gives the following equation, $AsO_5 + 5HS = AsS_5 + 5HO$, as expressing the reaction. H. Ludwig (*Arch. Pharm.*, 1859, **147**, 32—34) quotes Wackenroder's "Dictate of Forensic Chemistry," in which the latter says that the arsenic acid is first reduced by hydrogen sulphide to arsenious acid, even in the presence of hydrochloric acid, and that then a mixture of arsenic trisulphide and sulphur is precipitated. H. Rose (*Handbuch*, 1851, 383) finds that on dissolving this precipitate in ammonia and adding silver nitrate, brown silver arsenate is thrown down, whereas arsenic trisulphide, free from sulphur, when similarly treated, yields yellow silver arsenite. Otto (*Lehrbuch*, 2 ed., 1019), Fresenius (*Anleitung*, 1856), Will (*Anleitung*, 1857), and Wicke (*Analyse*, 1857) express the opinion that the precipitate formed by the action of hydrogen sulphide on arsenic acid solutions is arsenic pentasulphide. Ludwig (*loc. cit.*) finds that in the above reaction pale-yellow (!) sulphur is precipitated at first, and later on lemon-yellow arsenic trisulphide is thrown down; he expresses the reaction as follows:—

$$AsO_5 + 5HS = AsS_3 + S_2 + 5HO.$$

H. Rose (*Ann. Phys. Chem.*, 1859, **107**, 186), after passing hydrogen sulphide into a solution of arsenic acid, heated the solution and filtered off the separated sulphur. On adding silver nitrate to the filtrate, both the yellow silver arsenite and brown silver arsenate

* Read: Tomeetchek.

were thrown down; this afforded a proof that a partial reduction to arsenious acid had taken place. The precipitate formed by the continued action of hydrogen sulphide on arsenic acid is regarded by Rose as a mixture of arsenic trisulphide with sulphur, and from analogy the conclusion is drawn that antimony pentasulphide as well as arsenic pentasulphide may exist in combinations as double sulphides, but *not in the free state*. Since that time, the reaction in question is represented in Manuals of Chemistry, as follows:—

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

We cannot but remark that all the experiments quoted above have been *qualitative* merely, the products of reactions were not analysed, neither was the reaction in any way studied quantitatively.

In the year 1878, Bunsen (*Annalen*, **192**, 305—328) showed that on passing a rapid current of hydrogen sulphide into a solution of an alkaline arsenate, acidified with hydrochloric acid, and heated in a water-bath, arsenic pentasulphide was formed, and that this was the best mode of determining arsenic acid quantitatively. L. M. McCay (*Chem. News*, **54**, 287, and Abstr., 1887, 213) confirms Bunsen's results.

In spite of Bunsen's work, only a very few Manuals of Chemistry published since (especially analytical ones) seem to have taken notice of the possibility of a different action of hydrogen sulphide on arsenic acid.

Having regard to the discrepancies existing between the statements of Berzelius and Bunsen on the one hand, and those of Wackenroder, Ludwig, and Rose, on the other, we have investigated this subject more thoroughly.

First Series: Acid Solutions of Arsenates.

Three grams of arsenic trioxide were weighed exactly, dissolved in an aqueous solution of 100 grams of potassium hydroxide, and treated first with chlorine, and then with hydrochloric acid as described by Bunsen. The acid solution thus obtained was made up to one litre with distilled water (hereafter called "solution A"). The hydrogen sulphide used for the precipitation was prepared either from a material containing no arsenic, or by Jacobsen's method (*Ber.*, **20**, 1999), passing the gas through glass-wool impregnated with iodine, and washing with water (or still better with potassium sulphide solution), so as to purify the gas.

I. 100 c.c. of the "solution A" (= 0·3 gram As_2O_3 in the form of arsenic acid) was precipitated as arsenic pentasulphide in order to test the exactness of Bunsen's method; all the precautions described by Bunsen were carefully observed. The solution was diluted with

50 c.c. of water, and the small beaker containing it was placed in a large one filled with water at 60°. Hydrogen sulphide, the velocity of which was limited in this and the subsequent experiments to 5—6 bubbles per second, was passed through the liquid for three hours at 60°, and then, while the liquid cooled, for 12 hours. The first turbidity appeared after 3 minutes, the first precipitate after 5 minutes. After 24 hours, the precipitate was collected on a weighed filter, and washed well with water, alcohol, and carbon bisulphide,* it was then dried at 107°, and weighed until the weight became constant.† The weight of the precipitate was 0·4701 gram. Theory requires from 0·3 gram As_2O_3 : 0·47014 arsenic pentasulphide.

	Calculated.	Found.
Pentasulphide....	0·4701 gram.	0·4701 gram.

II. "Solution A" = 100 c.c. Water 50 c.c. Temp. 17°. First turbidity in 15 minutes, first precipitate in 30 minutes. Hydrogen sulphide passed for 24 hours. Weight of precipitate, 0·4599 gram. Theory requires 0·4701 gram; the precipitate, therefore, either consists partly of trisulphide, or the precipitation is incomplete. The last was shown to be the case, for, on continuing to pass the gas at 60°, 0·0106 gram more of pentasulphide was obtained. The sum of both weights equals the theoretical quantity calculated for the pentasulphide:—

	Calculated.	Found.
Pentasulphide....	0·4701 gram.	0·4705 gram.

From this experiment, it will be seen that arsenic pentasulphide is precipitated by hydrogen sulphide, not only from a hot but also from a cold solution of an alkaline arsenate containing an excess of hydrochloric acid. But precipitation in the cold is not practicable for analytical purposes, as it requires much time, and, moreover, is incomplete even after the gas has been passed for a long time; it was found here that, after 24 hours' treatment, 2·25 per cent. of the pentasulphide remained in solution.

* The filter was weighed in a thin glass bottle, but as its weight continually changes while in the desiccator and on the balance, another thin glass bottle containing a filter which had been treated precisely like the first one, was used as a counterpoise. The action of humidity on both filters being the same, this source of error was eliminated.

† Arsenic pentasulphide is, according to Bunsen, quite insoluble in water, alcohol, and carbon bisulphide, but sometimes, on pouring alcohol on the finely divided precipitate, slight traces are carried mechanically through the filter, as can be shown by evaporating the alcoholic filtrate and testing it for arsenic by Babo and Fresenius' method. In all cases, however, the quantity lost is less than the inevitable experimental errors.

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III. This experiment was made like No. II. Temperature 24°. Volume of "solution A," 130 c.c., of water, 50 c.c. After 24 hours, 0·4719 gram was precipitated, and from the filtrate at 60°, 0·003 gram of pentasulphide = 0·63 per cent., was obtained.

IV. In order to prove that the precipitate obtained *at the ordinary temperature* is really arsenic pentasulphide (from a mixture of trisulphide and sulphur, the latter can be extracted by means of carbon bisulphide), 500 c.c. of the "solution A" was treated for 36 hours at 17°, with an excess of hydrogen sulphide, the precipitate obtained washed completely with cold water, and then most carefully with large quantities of freshly distilled carbon bisulphide, so as to remove every trace of free sulphur; it was finally dried at 107°. Arsenic pentasulphide as thus prepared in the cold is of a pale lemon-yellow colour, and more finely divided than that precipitated from a warm solution. The dry sulphide cannot be powdered, since it becomes so strongly electric by friction that it is thrown about on all sides.

The following results were obtained on analysis:—

(*a*.) 0·6094 gram treated with nitric acid and potassium chlorate, and then evaporated with hydrochloric acid, gave 0·0297 gram sulphur (= 4·874 per cent.), and after the usual purification of the calcined impure barium sulphate, 2·0717 gram of the pure sulphate (= 46·746 per cent.).

(*b*.) 0·5303 gram of the sulphide, treated in a similar way, yielded 0·0472 gram sulphur (= 8·901 per cent.) and 1·6469 gram barium sulphate (= 42·702 per cent.).

The quantity of arsenic contained in arsenic pentasulphide, prepared at the ordinary temperature, may be calculated directly from Experiment II, representing a partial synthesis of that compound.

(*c*.) 0·3 gram As_2O_3, containing 0·2272 gram arsenic, yielded 0·4705 gram of arsenic pentasulphide.

	Calculated.		Found.			
			a.	*b*.	*c*.	Mean.
As_2..	150·0	48·34	(48·38)	(48·40)	48·30	48·36
S_5...	160·3	51·66	51·62	51·60	(51·70)	51·64
	100·0	100·00	100·00	100·00	100·00	100·00

In a similar way, the composition of arsenic pentasulphide obtained from a *warm* solution, may be calculated from the data of Experiment I.

0·3 gram of As_2O_3 gave 0·4701 gram arsenic pentasulphide.

	Theory and experiment.
Arsenic	48·34
Sulphur	51·66
	100·00

From this, it will be seen that under the aforesaid conditions arsenic pentasulphide is thrown down by hydrogen sulphide from a solution of potassium arsenate containing an excess of hydrochloric acid, both at low and high temperatures, and that no reduction takes place.

Second Series. Solutions of Pure Arsenic Acid.

Pure arsenic acid was next investigated. This was prepared by the action of nitric acid on pure arsenic trioxide; the oxidation was carried on in such a way that all loss by spirting was avoided, a small flask being used, which was closed by a glass tube bent several times and furnished with three bulbs; these were filled with nitric acid, through which the evolved gases escaped. The solution was then repeatedly evaporated down with water until all traces of nitric acid were expelled; 5·0 grams of vitreous arsenic trioxide, treated in this way and diluted with water, yielded 500 c.c. of "solution B."

The behaviour of the aqueous solution of arsenic acid towards reducing agents in general was next investigated.

Bunsen (*loc. cit.*, 321) took an arsenic acid solution, prepared from 0·1913 gram arsenic trioxide by the action of potassium hydroxide, chlorine, and hydrochloric acid, mixed it in a covered beaker with 100 c.c. of saturated sulphurous acid, and heated moderately for 20 hours. After removing the excess of sulphur dioxide by a current of air, the solution was precipitated with hydrogen sulphide. The precipitate was found to contain 51·27 parts of pentasulphide for 48·17 parts of trisulphide. In spite of the continued action of sulphurous acid, only about half of the arsenic acid was reduced.

We have repeated the experiment with a solution of pure arsenic acid.

V. 50 c.c. of "solution B" (= 0·5 gram As_2O_3) was treated exactly in the manner described, at 60° C. for 20 hours. The weight of the orange-yellow precipitate obtained was 0·6209 gram. Arsenic pentasulphide obtained from the above quantity should weigh 0·7836 gram; the trisulphide, 0·6216 gram. As the filtrate was free from arsenic, the precipitate was pure trisulphide.

	Calculated.	Found.
Arsenic trisulphide	0·6216 gram.	0·6209 gram.

It can readily be seen from a comparison of Bunsen's experiment

with ours, that under the conditions described free arsenic acid is completely reduced by sulphurous acid, and that the quantity reduced is much larger than in the case of a hydrochloric solution of an arsenate.

The object of the following experiments was to ascertain whether free arsenic acid is reduced by hydrogen sulphide, and whether it is precipitated more easily than hydrochloric solutions of an arsenate. If a current of hydrogen sulphide is passed, not too slowly, into an aqueous solution of arsenic acid at the ordinary temperature, it becomes opalescent after 5—15 minutes, according to its concentration, and then turns milky, but the precipitate, which at first resembles finely-divided sulphur, very soon becomes pale lemon-yellow, and is sometimes semi-transparent, especially if the reaction takes place at a temperature only a few degrees above zero; the same phenomenon is observed on adding a large quantity of saturated aqueous hydrogen sulphide to a dilute arsenic acid solution. This lemon-yellow, milky solution passes completely through a filter, and every trace of it may be washed out by water. As the precipitate is of the same colour, and as will be seen below, is also of the same composition as arsenic pentasulphide, it may be assumed that a new *colloïdal modification* of arsenic pentasulphide is formed, especially at a low temperature, the formation of colloïdal trisulphide taking place under similar conditions. At a certain degree of dilution, there is no perceptible distinction between liquid and precipitate in the pale greenish-yellow milky fluid, even after it has been allowed to remain for many days at a low temperature (2—4°). At the ordinary temperature, however, a separation of the precipitate from the liquid sometimes takes place a little less slowly, but the two cannot be separated by filtration. On adding an acid or a salt solution, a flocculent precipitate separates, especially on gently warming; it is now insoluble in water, and may be collected and washed in the ordinary way.

The following experiments show what products are formed by the continued action of hydrogen sulphide on arsenic acid:—

VI. 50 c.c. of arsenic "solution B" (= 0·5 gram As_2O_3) was diluted with 50 c.c. of water and a rapid current of hydrogen sulphide passed into it at 16—18°. The lemon-yellow colour of the precipitate after several hours changes to orange, showing that it is partly converted into arsenic trisulphide. After 48 hours, the action of the gas was interrupted, and then 10 c.c. of strong hydrochloric acid and 100 c.c. of ammonium chloride solution (10 parts to 100 H_2O) were added, in order to cause the aggregation of the precipitate and render it capable of being collected on a filter; after gently warming, the precipitate separates completely. As it contains a comparatively large amount of free sulphur, it must be washed most carefully and repeatedly with

carbon bisulphide; for this purpose, the lower part of the funnel is temporarily closed, then carbon bisulphide is poured on to the filter and allowed to run through; this operation is repeated six to eight times, so that on the whole the precipitate remains in contact with the carbon bisulphide for about half an hour. The results of incomplete washing with carbon bisulphide on the precipitate are seen from Experiments VII and VIII.

The weight of the precipitate obtained in the manner described above, was 0·7606 gram. From the filtrate, 0·001 gram of pentasulphide was obtained; this shows that, even after 48 hours, the precipitation of the free acid is incomplete, 0·13 per cent. remaining in solution.

The total quantity of the precipitate was 0·7616 gram (*a*). 0·5 gram arsenic trioxide should furnish 0·78358 gram (*b*) pure pentasulphide, but only 0·62165 gram (*c*) trisulphide. A simple calculation* shows that both sulphides are contained in the precipitate in the following proportion:—

Arsenic pentasulphide	86·43
Arsenic trisulphide	13·57
	100·00

The two following experiments show that *simple washing* with carbon bisulphide—which may be used with advantage for the extraction of the small quantity of sulphur precipitated along with the pure pentasulphide—is insufficient when the precipitate consists partly of a mixture of trisulphide with sulphur or when the quantity of free sulphur is somewhat larger.

VII. 50 c.c. of the acidified arsenate "solution A" was mixed with a solution of 1 gram of crystallised ferric chloride, and precipitated with hydrogen sulphide at 60°. The ferrous chloride formed had no reducing action on the arsenic acid. The precipitate of arsenic pentasulphide and sulphur was washed four times with carbon bisulphide in the ordinary rapid way. After drying, its weight was 0·2604 gram instead of 0·2350 gram, and after renewed extraction

* The percentage of the trisulphide is $\frac{100(b-a)}{b-c}$, the difference between that and 100 being pentasulphide. This method of calculation, as also that founded on the estimation of sulphur in the mixed sulphides, are the only trustworthy methods of deciding whether the precipitate consists of trisulphide, pentasulphide, or a mixture of both, supposing that the sulphur formed by the oxidation of hydrogen sulphide does not contain the "insoluble" modification. Rose's test mentioned above does not answer the purpose so well, for when small quantities of trisulphide are present, as is shown by the synthesis or analysis, no precipitate of silver arsenite is formed.

0·2548 gram: so that of the 0·0591 gram sulphur, formed by the action of hydrogen sulphide on the ferric chloride, 0·0198 gram remained undissolved, probably in the form of "insoluble" sulphur, which, according to Selmi (*Gmelin-Kraut's Handbuch*, 6th edition, **1**, Part II, 166) is formed by the action of hydrogen sulphide on ferric chloride.

VIII. 50 c.c. of "solution B" was precipitated at 80° in exactly the same manner as described below in Experiment X. After rapidly washing with carbon bisulphide (four times), the weight of the precipitate was 0·7792 gram instead of the 0·7618 gram obtained in Experiment X, when extraction was complete; 0·0174 gram of sulphur, therefore, remained undissolved.

IX. The preparation of the mixed sulphides was carried on at 4°, The precipitate, washed and dried, was analysed.

(*a.*) 0·3322 gram gave 1·212 gram $BaSO_4$ = 50·173 per cent. sulphur.

(*b.*) 0·7675 gram gave 2·8 grams $BaSO_4$ = 50·176 per cent. sulphur.

Mean = 50·175 per cent. sulphur.

Arsenic trisulphide contains 39·069 per cent. sulphur: the pentasulphide 51·66 per cent. The percentage composition of the mixture of sulphides as calculated* is—

Pentasulphide	85·57
Trisulphide	14·43
	100·00

It will be seen that both methods of calculation give one and the same result.

X. 50 c.c. of the arsenic "solution B," mixed with 50 c.c. water, was precipitated in the usual manner at 40°. After adding 10 c.c. hydrochloric acid and 100 c.c. of ammonium chloride solution (1 : 10), the last traces of pentasulphide remaining in solution were thrown down at 40°. Weight of precipitate, 0·7589 gram; composition—

Pentasulphide	84·76
Trisulphide	15·24
	100·00

XI. Solution B, 50 c.c.; water, 50 c.c.; temperature, 80°. First of all a lemon-yellow precipitate of pentasulphide was formed, then the trisulphide separated out on the surface of the liquid in the form of

* See footnote, p. 151.

orange, crystalline crusts. Hydrogen sulphide was passed for six hours at 80°, and for 24 hours at 18°. After the addition of 100 c.c. ammonium chloride solution, the precipitate was collected; its weight was 0·7575 gram. The filtrate was mixed with 25 c.c. hydrochloric acid and precipitated at 80°, when 0·0043 gram of pentasulphide was obtained. This shows that even after the continued action of hydrogen sulphide on the warm and cold pure arsenic acid solution, 0·56 per cent. of pentasulphide remained unprecipitated.

The total precipitate was 0·7618 gram; its composition—

Pentasulphide	86·56
Trisulphide	13·44
	100·00

It will be seen from the experiments VI, IX, X, and XI that the action of hydrogen sulphide on pure arsenic acid solutions between 4° and 80° is accompanied by a *partial* reduction of the arsenic acid to arsenious acid, and that by the further action of hydrogen sulphide a mixture of arsenic pentasulphide and trisulphide is formed, the quantity of trisulphide varying between 13·44 and 15·24 per cent. The variation of temperature does not seem to have any influence on the composition of the precipitate.

Third Series. Arsenic Acid in the Presence of a Salt.

XII. 50 c.c. of arsenic acid solution B was mixed with 100 c.c. of aqueous ammonium chloride solution (1 : 10), and treated with hydrogen sulphide at 17°. Heating to 70° did not cause complete precipitation, for 0·0271 gram was obtained from the filtrate by the action of the gas in presence of 10 c.c. of hydrochloric acid; the weight of the precipitate first obtained was 0·7221 gram. It will be seen that the precipitation in the presence of ammonium chloride is less complete than in the case of pure arsenic acid solution, 3·62 per cent. being left in the filtrate. From the total weight of the precipitate obtained = 0·7492 gram, the following percentage composition of the precipitate was calculated :—

Pentasulphide	78·77
Trisulphide	21·23
	100·00

XIII. This experiment was made in the same way with 0·5601 gram of arsenic trioxide oxidised to arsenic acid; temperature 40°. Only the portion precipitated after 24 hours was collected; its weight was 0·7625 gram. Assuming the same percentage composition of the

precipitate as in XII, the quantity of the sulphides thrown down is 90·85 per cent., 9·15 per cent. remaining in solution.

XIV. The same quantity of arsenic acid as in XIII was treated at 8° with hydrogen sulphide in the presence of ammonium chloride for 24 hours. Weight of precipitate: 0·8085 gram = 96·33 per cent. of mixed sulphides, 3·57 per cent. remaining in solution.

XV. Arsenic acid solution B, 50 c.c.; ammonium chloride solution, 100 c.c.; temperature, 70°. Hydrogen sulphide after 15 minutes produced a pure white precipitate of sulphur which soon became lemon-yellow, and after 30 minutes an orange precipitate was formed. From this moment the quantity of precipitate increased so rapidly that, after one hour, the voluminous precipitate settled well from the clear solution, and nothing more was thrown down by the further action of the gas. Five drops of hydrochloric acid were then added, and 10 c.c. after 15 minutes, in order that all the arsenic might be thrown down by the hydrogen sulphide. The passage of the gas was continued while the liquid was cooling, and after 12 hours it was interrupted. After completely extracting the free sulphur with carbon bisulphide, the weight of the precipitate, dried as usual at 107°, was found to be 0·7018 gram. Its composition is—

Pentasulphide	49·50
Trisulphide	50·50
	100·00

It is evident from these experiments, that in the presence of ammonium chloride hydrogen sulphide reduces the arsenic acid more than in the case of pure arsenic acid solution, and that the reduction increases with rise of temperature, 56·25 per cent. of the total arsenic present being converted into the trisulphide at 70°. On the contrary, the precipitation is far less complete than that of the pure acid.

Fourth Series. Arsenic Acid in Acid Solution.

XVI. 20 c.c. of the arsenic acid "solution B" was mixed with 50 c.c. of water and 20 c.c. of hydrochloric acid. Hydrogen sulphide was passed in at 17°. After 24 hours, the traces of arsenic still remaining in solution were thrown down by heating the solution to 70°; it was filtered after a lapse of two days. The colour of the precipitate was lemon-yellow, and identical with that of pentasulphide, and its weight was 0·7833 gram, that calculated for the pentasulphide being 0·7836 gram. From this partial synthesis, the composition of the pentasulphide is again calculated to be—

	Calculated (theory).	Found.
Arsenic	48·34	48·36
Sulphur.....	51·66	51·64
	100·00	100·00

XVII. Arsenic acid was prepared from 0·6970 gram trioxide, dissolved in water, 10 grams of ammonium nitrate, and 10 c.c. of hydrochloric acid were added, and the mixture precipitated at 75°. The weight of the precipitate was 1·0905 gram, that calculated for arsenic pentasulphide being 1·0923 gram.

XVIII. A solution of arsenic acid was precipitated with hydrogen sulphide at 10° in presence of ammonium nitrate and hydrochloric acid. The analysis of the precipitate, formed after 12 hours, and dried at 107° (after extraction with bisulphide of carbon), gave the following result:—

(*a.*) 0·2745 gram sulphide yielded 1·0305 gram barium sulphate.
(*b.*) 0·4 gram sulphide yielded 1·4975 gram barium sulphate. The precipitation took place at 4°.
(*c.*) 0·505 gram sulphide yielded 1·901 gram barium sulphate.

		Found.		
	Calculated.	*a.*	*b.*	*c.*
Arsenic	48·34	—	—	—
Sulphur	51·66	51·62	51·48	51·76
	100·00			

XIX. This experiment was made at 10°, in presence of ammonium nitrate, with a small quantity of hydrochloric acid only.

On analysis, 0·4757 gram sulphide gave 1·765 gram $BaSO_4$; this corresponds with 51·02 per cent. sulphur, showing that the pentasulphide is not pure, but that it contains some trisulphide; its composition is—

Pentasulphide	93·66
Trisulphide	6·34
	100·00

The foregoing experiments were varied in different ways, but the quantity of hydrogen sulphide passing through the liquid was kept as nearly as possible constant, in order to obtain results comparable among themselves with regard to the quantity of that gas employed.

The number of gas-bubbles was regulated, so that about 300 passed per minute.

The question now arose: How will a solution of arsenic acid, which yields *pure arsenic pentasulphide* when treated with an excess of hydrogen sulphide, behave, if the quantity of gas passing through the solution is *much smaller* in the unit of time? For the purpose of settling this point, the following experiment was made.

XX. To 100 c.c. of "solution A" (which served for experiments I—IV, and contains 0·3 gram arsenic trioxide in the form of potassium arsenate in a solution strongly acid with hydrochloric acid) 50 c.c. of water was added, and the mixture heated at 70°. A current of hydrogen sulphide was passed through the liquid as slowly as possible, that is, at the rate of 20—25 bubbles per minute. The precipitate formed after 20 minutes was nearly white, and after 30 minutes orange crusts of trisulphide were formed on the surface of the liquid. At the same time, a turbidity caused by the pale-yellow pentasulphide made its appearance in the liquid. After 5 hours, the precipitation was complete; the gas, however, was passed into the liquid for 12 hours more, while the liquid was cooling. The weight of the precipitate formed was 0·4413 gram; its composition was—

Arsenic pentasulphide	70·31
,, trisulphide	29·69
	100·00

From this it follows that the hydrochloric solution of an arsenate (which is reduced less readily than a pure arsenic acid solution both by sulphurous acid and by hydrogen sulphide), when warmed is reduced by hydrogen sulphide more completely if the gas is present in small quantity.

It may be concluded from analogy, with regard to the *second* and *third* series of experiments, that the reduction of arsenic acid solutions, either pure or containing ammonium chloride, will be more complete the more slowly the hydrogen sulphide is passed through the solution.

It follows further from the whole four series, that arsenic acid is not reduced by hydrogen sulphide if the solution contains enough hydrochloric acid, or of this acid and a salt, the gas being present in excess, and that it behaves towards hydrogen sulphide exactly like a solution of an alkaline arsenate acidified with hydrochloric acid. When, however, the quantity of hydrochloric acid is small in proportion to the ammonium salt, a little arsenic acid is reduced, and some trisulphide is precipitated along with the pentasulphide. When no hydrochloric acid is present, the phenomena described in experiments XII—XIV take place.

The following is the result of the experiments described in the present communication:—

On acting with hydrogen sulphide on aqueous arsenic acid or acid solutions of arsenates, it is shown, *cæteris paribus*—

1. That more *arsenic pentasulphide* is formed—

(*a.*) The larger the quantity of hydrochloric acid present;
(*b.*) The larger the quantity of hydrogen sulphide passed in the unit of time; and
(*c.*) The lower the temperature (between 0—100°).

2. That *arsenic trisulphide* mixed with sulphur is formed in larger quantity (in consequence of the reducing action of the hydrogen sulphide)—

(*a.*) The less hydrochloric acid there is present;
(*b.*) The smaller the quantity of hydrogen sulphide; and
(*c.*) The higher the temperature.

3. Arsenic acid, especially in presence of ammonium chloride, is reduced more easily than an acidified solution of an arsenate.

4. The *second limit*, namely, complete formation of *trisulphide*, is reached, if at all, with greater difficulty than the *first limit*, that is formation of pure *pentasulphide*. Probably the relation between the mode of formation of the two sulphides and the conditions described above may be represented by an asymptotic curve, but at present the principal function, the quantity of hydrogen sulphide coming into contact and reaction with the liquid in the unit of time, cannot be expressed mathematically.

Discussion of Earlier Experiments on this Reaction.

Berzelius' statement that arsenic pentasulphide is precipitated from aqueous arsenic acid solutions by hydrogen sulphide, is correct only from the qualitative point of view, that is, only as far as it represents the main reaction, when no foreign substance is present. It is perfectly correct, however, as regards hydrochloric solutions of arsenic acid, or solutions of alkaline arsenates in presence of an excess of hydrogen sulphide. (This was not mentioned by Berzelius.)

The statements of Wackenroder and of Ludwig are correct only with respect to the secondary reaction between hydrogen sulphide and arsenic acid. Both these chemists, as was stated before, have investigated the reaction qualitatively only, and both have overlooked the fact that their "pale-yellow" (Wackenroder) or "light grey-yellow" (Ludwig) sulphur was nothing else than *arsenic pentasulphide*. The said secondary reaction is still less marked when hydrochloric acid is present.

H. Rose's observation that, when hydrogen sulphide acts for a short

time only on aqueous arsenic acid, *partial* reduction of the latter takes place, is correct. But Rose overlooked the fact that his milky precipitate of sulphur (which, as he says, is never free from arsenic) consists to a great extent of (colloïdal) arsenic pentasulphide. We have several times repeated the experiment as described by Rose qualitatively, that is, under varying conditions, and we found that in all cases a mixture of arsenic trisulphide and pentasulphide was produced. Rose himself gives neither a qualitative nor a quantitative proof that the precipitate he obtained was actually arsenic trisulphide mixed with sulphur, and his conclusion that the pentasulphides of arsenic and also that of antimony cannot exist in the free state, may be regarded as untenable.

Regarded as an analytical operation, the following conclusions may be drawn from Bunsen's experiments and our own on the reaction between hydrogen sulphide and arsenic acid.

Solutions of arsenic acid or of soluble arsenates are tested qualitatively (by students), by precipitating with hydrogen sulphide, as a rule in the presence of hydrochloric acid. The following notes, therefore, might be inserted with advantage in Manuals of Analytical Chemistry :—

When a *rapid current* of hydrogen sulphide is passed into a solution of arsenic acid, *arsenic pentasulphide* alone is formed, although but slowly, if free hydrochloric acid is present, and the liquid is kept warm :—

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O.$$

When the gas is *passed slowly* into a solution of the free acid, or into warm acid solutions of arsenates, a secondary reaction takes place in two stages, along with the primary reaction mentioned above :—

$$(a.)\ H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O.$$
$$(b.)\ 2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

For the quantitative estimation of arsenic acid in the form of a sulphide, it is best to convert it into *pentasulphide*, and for this purpose Bunsen's method must be *strictly adhered to*. In the case of free arsenic acid, the precipitation with hydrogen sulphide must be carried on in the presence of a sufficient quantity of hydrochloric acid.

We are unable to answer satisfactorily the question as to why, in the reaction studied in the present paper, arsenic pentasulphide alone is formed under one set of conditions, whilst under other conditions both pentasulphide and trisulphide are formed simultaneously, the proportion of the latter being sometimes very considerable. It is no explanation to say, for example, that if a *small* quantity of hydrogen

sulphide is present, part of it is oxidised by the arsenic acid, but that this does not occur if the gas is present in *excess*, or that the oxidation of hydrogen sulphide by arsenic acid (or the reduction of the latter) does not take place as easily in presence of hydrochloric acid as it does in the case of pure arsenic acid, &c.; the above question, therefore, remains an interesting problem of chemical dynamics. It may be that the molecular state in which arsenic acid exists under the different conditions affects the reactions in some way.

XIII.—NOTES FROM THE CHEMICAL LABORATORY OF THE YORKSHIRE COLLEGE.

No. I. *Reduction of Potassium Dichromate by Oxalic Acid.*

By C. H. Bothamley, Assistant Lecturer on Chemistry in the Yorkshire College.

In the course of a technical investigation, my attention was attracted by a reaction which takes place between solid potassium dichromate and crystallised oxalic acid even at the ordinary temperature. It is of course well known that these substances react in solution, but a reaction between the solid compounds does not appear to have been observed; and since they are both largely used in chemical industries and are not unfrequently stored side by side, the nature of the reaction is not without interest.

The oxalic acid used was purified by recrystallisation and dried by exposure to air; the potassium dichromate was recrystallised, dried, and carefully fused. When the two substances are finely powdered and intimately mixed, the reaction takes place spontaneously at the ordinary temperature after two or three hours. If the mixture is heated to 30—35°, an energetic and almost instantaneous reaction takes place. The mass becomes semi-liquid, swells up, and becomes almost black, and carbonic anhydride and water vapour are given off in large quantity. There is considerable development of heat, and in some cases the temperature was observed to rise to 90°.

When 4 parts of oxalic acid are mixed with 1 part of potassium dichromate, the oxalic acid being in considerable excess, the reduction of the dichromate is complete, and the product forms a deep purple solution identical with that obtained by reduction in an aqueous solu-

tion. When, however, the dichromate is in excess, the result of the reaction is different. Experiments were made with two mixtures, the first (A) containing equal weights of the two substances, and the second (B) 2 parts of potassium dichromate to 1 part of the crystallised acid. The compounds were separately powdered as finely as possible, and then thoroughly mixed. Two sets of experiments were made with each mixture. In one, the mixture was heated at 110—120° until the weight was constant, and the loss of weight was determined. The total loss observed is due to the complete dehydration of the acid and its partial oxidation by the dichromate. The loss from dehydration is readily calculated, and the difference is the loss due to oxidation. The residue is dark-coloured and friable, and is completely soluble in water, forming a dark olive-brown solution; this has a distinctly acid reaction to litmus, and deposits neither precipitate nor crystals on standing. It contains a chromate, a chromic salt, and oxalic acid or an oxalate, and is essentially a solution of chromic oxalate mixed with potassium chromate and dichromate and some unaltered free oxalic acid. Possibly the dichromate partially decomposes the chromic oxalate with formation of a chromic chromate, which remains in solution in presence of the free oxalic acid. If the solution is mixed with ammonia, a brown precipitate of chromium chromate is formed. The chromium existing in the liquid as a chromic salt was determined by boiling with a slight excess of sodium hydroxide, and the oxalic acid in the filtrate was precipitated with calcium chloride after acidifying with acetic acid.

A. A mixture of equal parts of potassium dichromate and oxalic acid.

(1.) 6·194 grams (= 3·097 $H_2C_2O_4{\cdot}2H_2O$) at 110—120° lost 2·185 grams. Loss due to oxidation = 1·300.

Complete oxidation : actual oxidation : : 100 : 50.

Chromic oxide formed 0·623 gram, whence $6(H_2C_2O_4{\cdot}2H_2O) = Cr_2O_3$.

(2.) 4·940 grams (= 2·470 acid, at 110—120° lost 1·774 gram. Loss due to oxidation 1·068.

Complete oxidation : actual oxidation : : 100 : 51.

Chromic oxide formed 0·475. Calc. 0·497.

(3.) 4·993 grams (= 2·497 acid) at 110—120° lost 1·796 gram. Loss due to oxidation 1·083.

Complete oxidation : actual oxidation : : 100 : 52.

Chromic oxide obtained = 0·491. Calc. 0·503.

Oxalic acid left = 1·360.

Acid taken : acid unoxidised : : 100 : 54.

(4.) 6·336 gram (= 3·168 acid) at 110—120° lost 2·290. Loss due to oxidation 1·385.

Complete oxidation : actual oxidation : : 100 : 52.

Oxalic acid left = 1·671.

Acid taken : acid unoxidised : : 100 : 53.

The facts that almost exactly half the oxalic acid remains unoxidised, and that 1 mol. of chromic oxide is obtained for 6 mols. of acid taken, indicate that the first stage of this reaction is represented by the equation $2K_2Cr_2O_7 + 6H_2C_2O_4 = Cr_2(C_2O_4)_3 + 6CO_2 + 6H_2O + 2K_2CrO_4$. The reaction is limited by the combination of the reduced chromic oxide with the unaltered oxalic acid to form chromic oxalate. The numbers actually obtained indicate that the reaction is not quite complete. The loss on oxidation, the proportion of chromic oxide formed, and the proportion of oxalic acid left, show that about 95 per cent. of the total theoretical decomposition has taken place.

In the second set of experiments, with the same proportion of dichromate and acid, the mixture was first heated at 110—120°, and then over a small flame to a temperature below visible redness, care being taken to avoid fusion. Further decomposition ensues, the mass becomes green, and on treatment with water, potassium chromate dissolves and chromic oxide is left. The solution contains no oxalic acid and no chromic salt.

(5.) 5·902 grams (= 2·951 of acid) lost 3·152 grams. Loss due to oxidation 2·309.

Complete oxidation : actual oxidation : : 100 : 93.

Chromic oxide formed 0·599. Calc. ($6H_2C_2O_4 = Cr_2O_3$) 0·594.

(6.) 4·084 grams (= 2·041 of acid) lost 2·201 grams. Loss due to oxidation 1·618.

Complete oxidation : actual oxidation : : 100 : 94.

Chromic oxide formed, 0·418. Calc. 0·411.

Since the observed loss is only 94 per cent. of that calculated on the assumption that the oxalic acid is oxidised to carbonic anhydride, it is evident that oxidation is not complete. Moreover, the proportion of chromic oxide obtained is but slightly higher than that formed at the lower temperature, and hence very little further reduction of the dichromate has taken place. It follows that in the second stage of the reaction the chromic oxalate formed at the lower temperature decomposes in accordance with the equation $Cr_2(C_2O_4)_3 = Cr_2O_3 + 3CO_2 + 3CO$. The numbers obtained agree well with the numbers calculated. The loss of weight should be 2·295 and 1·587 respectively, and the fact that the loss of weight and the proportion of chromic oxide are both slightly higher than the calculated values is due to a

slight further reduction at the higher temperature. The proportion of dichromate in the mixture is not much above that required by the first equation, and it will be seen that with an excess of dichromate the second stage of the reaction proceeds somewhat differently.

B. A mixture of potassium dichromate (2 parts) and oxalic acid (1 part).

(7.) 6·663 grams (= 2·221 acid) at 120° lost 1·601 gram. Loss due to oxidation = 0·966 gram.

Complete oxidation : actual oxidation : : 100 : 52.

Chromic oxide formed 0·427. Calc. 0·447.

Oxalic acid left = 1·170.

Acid taken : acid unoxidised : : 100 : 53.

(8.) 5·264 grams (= 1·755 acid) at 120° lost 1·264 gram. Loss due to oxidation 0·762.

Complete oxidation : actual oxidation : : 100 : 52.

Chromic oxide formed 0·336. Calc. 0·354.

Oxalic acid left 0·9499.

Acid taken : acid unoxidised : : 100 : 54.

It is evident that with these proportions the first stage of the reaction is the same as with equal proportions of the acid and dichromate, and proceeds to practically the same extent, notwithstanding the increased proportion of the oxidising agent. The decomposition is limited by the formation of chromic oxalate, which at 120° is not appreciably affected by the excess of dichromate.

When, however, the mixture is first heated at 110—120°, and then at a higher temperature, as in Series A, the result is different.

(9.) 6·818 grams (= 2·273 acid) lost 2·517 grams. Loss due to oxidation 1·867.

Complete oxidation : actual oxidation : : 100 : 98.

Chromic oxide formed = 0·8255.

(10.) 5·132 grams (= 1·711 acid) lost 1·891 gram. Loss due to oxidation = 1·402.

Complete oxidation : actual oxidation : : 100 : 97.

Chromic oxide formed = 0·6165.

In this case, oxidation in the second stage proceeds considerably further than in Series A, a result due to the presence of excess of dichromate. It is easy, in fact, to recognise the presence of dichromate in the aqueous solution of the residue. The greater loss and the formation of a further quantity of the chromic oxide indicate that at the higher temperature the excess of potassium dichromate acts

on the chromic oxalate in accordance with the equation $2K_2Cr_2O_7 + Cr_2(C_2O_4)_3 = 2Cr_2O_3 + 6CO_2 + 2K_2CrO_4$. The reaction is not quite complete, and some of the carbon escapes as carbon monoxide without reducing the dichromate, a result doubtless due to the fact that the proportion of dichromate is only slightly above that required by the equation. With a larger proportion of the salt, oxidation would be more complete. The complete oxidation of oxalic acid by excess of potassium dichromate at a temperature below a red heat is represented by the equation $4K_2Cr_2O_7 + 6H_2C_2O_4 = 2Cr_2O_3 + 6H_2O + 12CO_2 + 4K_2CrO_4$.

When carefully dehydrated oxalic acid is mixed with potassium dichromate, the phenomena are somewhat different from those observed with the hydrated acid. The reaction does not take place spontaneously at the ordinary temperature even after several days. If, however, the mixture is freely exposed to the air some decomposition ensues, doubtless owing to absorption of moisture from the air. When the mixture is heated to 30—35°, there is an almost instantaneous reaction. The mass does not become pasty, but forms a bulky, porous and friable grey product, totally different in appearance from that obtained with the hydrated acid. The difference in the appearance of the product, and the fact that the reaction does not take place spontaneously, are the more remarkable since when the decomposition is initiated by a rise of temperature, the nature of the reaction and the extent to which it proceeds are practically the same in both cases. With equal parts of the dichromate and dehydrated acid, however, some of the acid is volatilised unchanged, and hence experiments were made only with a mixture of 2 parts dichromate and 1 part of acid.

(11.) 3·164 grams (= 1·055 acid) at 120° lost 0·655 gram, the whole of the loss being due to oxidation.

Complete oxidation : actual oxidation : : 100 : 53.

Chromic oxide obtained 0·239. Calc. 0·236.

Oxalic acid left = 0·549.

Acid taken : acid unoxidised : : 100 : 52.

(12.) 5·603 grams (= 1·868 acid) at the higher temperature lost 2·050.

Complete oxidation : actual oxidation : : 100 : 94.

From these experiments it follows that—

(1.) Solid potassium dichromate and crystallised oxalic acid react spontaneously after two or three hours; or instantly at 30—35°, with great development of heat.

(2.) Potassium dichromate and dehydrated oxalic acid do not act spontaneously, but the reaction takes place instantly at 30—35°.

(3.) Part of the potassium dichromate is reduced, and the chromic oxide combines with unaltered oxalic acid to produce chromic oxalate, the formation of which limits the decomposition at 120°.

(4.) At a higher temperature chromic oxalate reacts with an excess of dichromate, forming chromic oxide, carbonic anhydride, and normal chromate.

(5.) The dehydration of the oxalic acid affects only the commencement of the reaction, but has no influence on the nature and limit of the decomposition.

No. II. *Estimation of Chlorates by means of the Zinc-copper Couple.*

By C. H. Bothamley and G. R. Thompson, Senior Brown Scholar.

In the estimation of chloric acid by means of the zinc-copper couple (Thorpe, *Jour. Chem. Soc.*, 1873, 541), the results are not unfrequently too low, and this is usually attributed to incomplete reduction. It was observed, however, that the deficiency is often considerable when the solution has been in contact with the couple for several hours, and in two instances in which the solution and the couple were allowed to remain in contact over night it was found to be practically impossible to extract all the chlorine from the residue by means of hot water, since the liquid used for a twenty-fifth washing gave a very distinct reaction for chlorides. It therefore seemed probable that part of the chlorine was converted into an insoluble compound, and the following experiments were made with a view to ascertain the magnitude of the error due to this cause.

The zinc-copper couple was made in a manner similar to that recommended by Gladstone and Tribe. Thin, granulated zinc was washed with sodium hydroxide solution, then with dilute sulphuric acid, and finally with water. It was then treated with two successive quantities of a 3 per cent. solution of copper sulphate heated to 30—40°, and the couple was carefully washed with distilled water. In this way, a spongy but adherent film is obtained. The bulk of the couple was such that it was first covered by the 25 c.c. of solution used for each determination. The reduced chloride was estimated by means of decinormal silver nitrate. The numbers given are in each case the mean of at least two concordant determinations.

A. 25 c.c. of solution contained pure $KClO_3$ equivalent to 0·0715 gram of Cl.

(1.) Heated to boiling 30 minutes: filtered and washed eight times with boiling water. Chlorine found = 0·0688: error −0·0027.

(2.) Heated gently for two hours: boiled half an hour; washed as before. Chlorine found = 0·0683: error −0·0032.

B. 25 c.c. contained $KClO_3$ equivalent to 0·0685 Cl.

(3.) Allowed to stand 15 hours: boiled half an hour: washed as before. Chlorine found = 0·0647: error −0·0038.

(4.) Allowed to stand 15 hours: boiled half an hour; washed twice with a small quantity of 3 per cent. sulphuric acid, and finally with water. Chlorine found = 0·0684: error −0·0001.

These experiments prove that, under the conditions described, from 4·0 to 5·5 per cent. of the total chlorine present is converted into a compound which is only slightly soluble in water, but is readily soluble in dilute sulphuric acid. Experiments were therefore made in order to determine the conditions affecting the formation of this insoluble compound.

After the chlorate solution (25 c.c.) had been heated with the couple and the liquid filtered, the residue was washed eight times with boiling water, and the chlorine in the aqueous filtrate was estimated. The residue was then treated with pure dilute sulphuric acid (3 : 100), washed with water, the filtrate neutralised with pure calcium carbonate, and titrated with the silver solution.

C. 25 c.c. contained 0·584 $KClO_3$, equivalent to 0·169 Cl.

	Cl in		Total Cl.
	Aqueous filtrate.	Acid washings.	
(5.) Boiled half an hour	0·153	0·015	0·168
(6.) Boiled one hour	0·161	0·008	0·169
(7.) Heated gently two hours: boiled half an hour....	0·159	0·009	0·168
(8.) Allowed to stand 15 hours: boiled half an hour....	0·164	0·005	0·169

D. 25 c.c. contained 0·1243 $KClO_3$, equivalent to 0·0360 Cl.

	Aqueous filtrate.	Acid washings.	Total Cl.
(9.) Boiled one hour.....	0·0341	0·0019	0·0360
(10.) Boiled one hour: allowed to stand three hours..	0·0338	0·0022	0·0360

On comparing these results, it will be seen that the proportion of chlorine rendered insoluble varies irregularly and bears no relation to the time of action. In all probability the character of the couple or, in other words, the rate at which reduction takes place, is an important factor. It is clear, however, that the quantity of insoluble chloride formed is much smaller in dilute solutions.

There can be little doubt that the insoluble substance is a zinc oxychloride. It is most probably the product of a secondary reaction either between the couple and the alkaline chloride formed, or between the zinc hydroxide and the alkaline chloride, for if a solution of potassium chloride is heated with a zinc-copper couple part of the chlorine forms an insoluble compound, though the proportion is not so great as in the reduction of the chlorate.

E. 25 c.c. containing potassium chloride equivalent to 0·1843 Cl.

	Aqueous filtrate.	Acid washings.	Total Cl.
(11.) Heated two hours: boiled half an hour	0·1800	0·0043	0·1843
(12.) Allowed to stand several days.....	0·1752	0·0081	0·1833

(13.) 25 c.c. of potassium chloride solution containing 0·0712 Cl were heated for two hours with a zinc-copper couple, and then boiled for half an hour; 0·0010 chlorine became insoluble.

In order to remove this source of error, the following mode of procedure has been adopted :—The solution should not contain more than 0·5 gram of potassium chlorate or the equivalent quantity of any other chlorate in 25 c.c. It is gently heated with the zinc-copper couple, which it should just cover, for half an hour, and is then boiled for half an hour. Pure dilute sulphuric acid is now carefully added until the precipitate of zinc hydroxide and oxychloride just dissolves, and the liquid is filtered, neutralised with pure precipitated calcium carbonate, and titrated in the usual manner.

The following results, obtained by students in the ordinary course of laboratory work, illustrate the accuracy of the method as thus modified :—

0·2704 gram $KClO_3$	gave	0·0781 gram Cl	: error	0·0001.
0·2015 „		0·0584 „	„	0·0001.
0·2165 „		0·0627 „	„	0·0000.

The conclusions drawn from these results may be summed up as follows :—

(1.) When potassium chlorate is reduced by means of a zinc-copper couple, part of the reduced chloride is converted into insoluble zinc oxychloride.

(2.) The proportion of oxychloride formed increases with the concentration of the chlorate solution.

(3.) The error due to this cause may be removed by slightly acidifying the liquid before filtration.

(4.) The deficiencies in the amount of chlorine found, which were formerly attributed to incomplete reduction, especially with concentrated solutions of chlorates, were really due to the formation of the insoluble oxychloride.

University of Michigan

XIV.—*The Alloys of Copper and Antimony and of Copper and Tin.*

By E. J. Ball, Ph.D., Assistant in Metallurgy at the Normal School of Science.

The investigation made by Mr. G. Kamensky,* of the electrical relations of the copper-antimony alloys shows that the curve of electrical resistance closely agrees with that of the copper-tin series, the highest point of the induction-balance curve being occupied by "Regulus of Venus," Cu_2Sb, and the lowest by an alloy which agrees in composition with the formula Cu_4Sb. This led to the belief that interesting results might be obtained by a further investigation of this series of alloys, especially as regards the two turning points of the curve, Cu_2Sb and Cu_4Sb. With this end in view, it appeared best to alloy together in varying proportions copper, antimony, and lead, as the latter, whilst yielding alloys with antimony which have properties intermediary between those of the constituents, does not under ordinary circumstances appear to alloy itself with more than about $3\frac{1}{2}$ per cent. of copper. It appeared probable, therefore, that separations of alloys of more or less definite composition might occur, the closer investigation of which might lead to interesting results.

In the first series of alloys prepared, the copper and antimony were always in the proportions that form "Regulus of Venus," nearly equal weights, and the alloys may therefore be considered as those of this substance with lead. The lead varied by quantities of 5 per cent. Thus the first alloy contained 95 per cent. of lead and 5 per cent. of Cu_2Sb; the second, 90 per cent. and 10 per cent. respectively; the

* *Proceedings of the Physical Society of London*, vol. vi, p. 53.

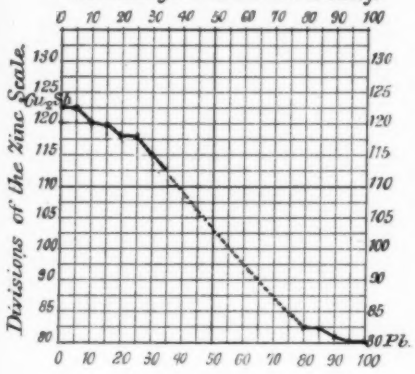
third contained 85 per cent. of lead; and the fourth 80 per cent. No alloy was obtained with 75 per cent. of lead and 25 per cent. of "Regulus of Venus;" the fused mixture separated into two layers on cooling, as did every other mixture, until the alloy containing 65 parts of "Regulus of Venus" and 35 parts of lead was reached, from which point to the "Regulus of Venus" itself the alloys appeared perfectly homogeneous.

The extensibility of the alloys of this series from lead to the alloy containing 20 per cent. of Cu_2Sb, varied with the percentage of the lead. The alloy with 80 per cent. of lead could be hammered, rolled, and cut with the knife, but when cast could be broken easily with the fingers. In colour, the purple tint of the "Regulus of Venus" was visible throughout that portion of the series containing over 65 per cent. of Cu_2Sb, only varying in intensity with the percentage present. This purple tint was just perceptible in the alloy with 80 per cent. of lead. The alloys forming the latter portion of the series were all highly crystalline and brittle. The mixture containing 60 parts of "Regulus of Venus" and 40 of lead separated, on cooling in a cylindrical mould, into two distinctly defined concentric cylinders. The outer cylinder was crystalline in structure and purple in colour; it proved on analysis to be Cu_2Sb, retaining 26 per cent. of lead. The inner cylinder was grey in colour, and had a granular fracture; it contained 80 per cent. of lead and 20 per cent. of Cu_2Sb, and as the alloy with this composition mentioned above was the one immediately preceding the separation of the fused mixture into two alloys, it seems probable that it represents the saturated solution of Cu_2Sb in lead. In order to determine the effect of the rate of cooling on this separation, Professor Roberts-Austen, to whom I beg to offer my thanks for the assistance and advice he has kindly afforded me throughout this investigation, caused the fused mixture to be cast in a square mould hollowed out in the centre of a brick. The mixture was allowed to cool very slowly, and was then found to have separated into two superimposed alloys similar in appearance to those previously observed.

All the intermediate alloys between the one with 80 per cent. of lead and the one with 35 per cent., which separated on cooling into two layers, were melted up together, and allowed to cool very slowly. When solidification had taken place, it was found that there had been a separation into three distinct alloys of different density. These were submitted to analysis, with the following results:—

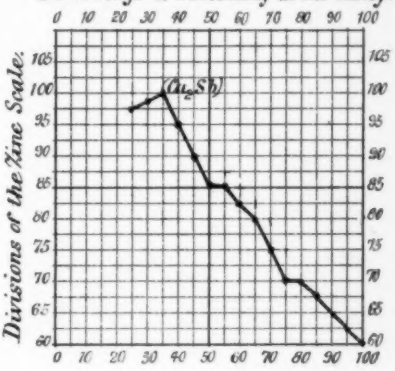
No. 1.

Percentage of Lead in the Alloy.



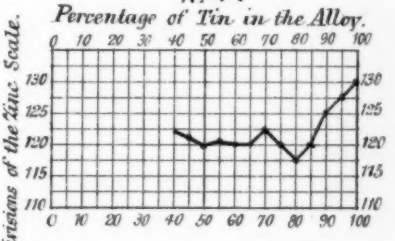
No. 2.

Percentage of Antimony in the Alloy.



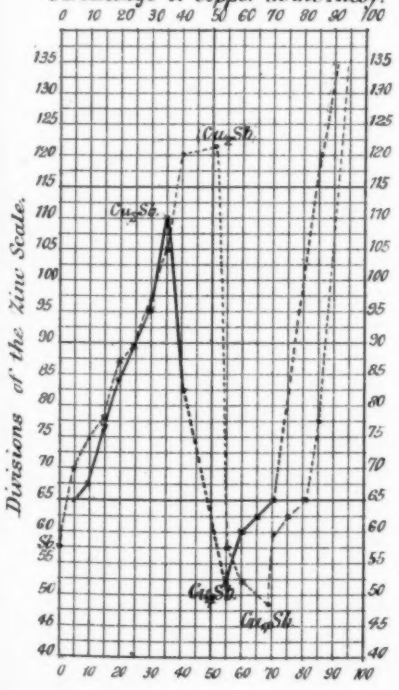
No. 4.

Percentage of Tin in the Alloy.



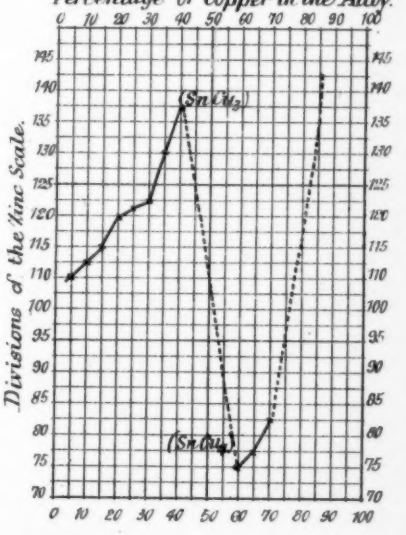
No. 3.

Percentage of Copper in the Alloy.



No. 5.

Percentage of Copper in the Alloy.



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	Upper alloy. Per cent.	Middle alloy. Per cent.	Lower alloy. Per cent.
Copper.....	67·43	47·37	7·57
Antimony.....	32·46	40·94	3·85
Lead.....	not determined	11·10	88·13
Totals	99·89	99·41	99·55

It will be observed that the composition of the upper alloy, of which there was relatively but a very small quantity, corresponds with the formula Cu_4Sb. The middle alloy more nearly approaches in composition to "Regulus of Venus," containing dissolved lead, and the lower alloy to lead containing dissolved Cu_4Sb, but the repeated fusions and castings to which the mixture had previously been subjected, had caused a portion of the antimony to be oxidised and lost.

In their physical characters, these three alloys differed widely from one another. The upper alloy, Cu_4Sb, was nearly white, and its fracture was vitreous. The middle alloy was of a blue-grey colour, and its fracture was conchoïdal. The lower alloy in appearance resembled lead.

The separation of the Cu_4Sb appears to point to its being a true compound. On fusing it with silver sulphide in varying proportions, it was found that nearly all the copper might be displaced by silver. Of the two alloys approaching in composition the formulæ $Cu_7Ag_2Sb_2$ and $Cu_6Ag_4Sb_2$, the former was of a lighter grey colour, and fused at a somewhat lower temperature than the latter. "Regulus of Venus," Cu_2Sb, was similarly treated, and with like results. These substituted alloys were of interest, as by substituting silver for the copper the colour was not greatly affected, the alloy approaching in composition the formula $Cu_3Ag_2Sb_2$, having nearly the same purple colour as the "Regulus of Venus."

In a second series of alloys, the ratio borne by the copper to the lead remained constant, that of the antimony varying. The composition of the first alloy of this series was 95 per cent. of antimony, 2·5 per cent. of lead, and 2·5 per cent. of copper; the second contained 90 per cent. of antimony, 5 per cent. of copper, and 5 per cent. of lead; and so on for the remainder of the series. The alloys were to all appearances homogeneous, until the one containing 25 per cent. of antimony was reached, the copper and antimony in which are almost in the proportions requisite for the formation of Cu_3Sb. After this point was passed, a large proportion of the lead separated out, leaving alloys rich in antimony and copper, but poor in lead. The alloys of this series varied in colour from white to grey. They were all more or less crystalline, and the fracture became conchoïdal as the series approached the alloy containing 25 per cent. of antimony.

In a third series, the relative quantities of antimony and lead remained constant. They were present in equal proportions. The copper, on the other hand, diminished 5 per cent. in each consecutive alloy. In this series of alloys, all formed except the one containing 50 per cent. of copper, 25 of antimony, and 25 of lead, which separated on cooling into an alloy which proved to be Cu_4Sb, and lead containing the excess of antimony and some dissolved Cu_4Sb.

The alloys of each of these three series were, as far as was possible, cast into discs, ground to the same size, and examined by the aid of the induction balance. The curve of electrical resistance so obtained proved in the case of the first series to be almost a straight line between the terminals, lead and "Regulus of Venus." This will be seen from Curve No. 1.

In the second series, there was a gradual rise from antimony to the alloy containing 35 per cent. of antimony (nearly Cu_2Sb), after which there was a slight drop. See Curve No. 2.

Allowing for the dilution of the alloys by lead, the curve of the third series was almost identical with that obtained by Kamensky in the case of the copper-antimony alloys without lead. The two curves are shown in Table No. 3, that of Kamensky being the one shown thus, ----- throughout.

The same mould was used in both these series, and the alloys were ground to about the same volume.

From these results, it would appear probable that the alloys agreeing in their composition with the formulæ Cu_2Sb and Cu_4Sb, are definite compounds, and that the copper-antimony alloys from copper to Cu_4Sb are mixtures of this compound with an excess of copper; that the alloys between Cu_4Sb and Cu_2Sb are mixtures of the two; and that the alloys between Cu_2Sb and antimony are mixtures of these two substances. It would also appear that lead is without influence on the copper-antimony alloys otherwise than by diluting them.

The copper-tin alloys were then treated in a similar manner, and the results are of interest, as they tend to support the evidence on this subject adduced by Mr. A. P. Laurie.

It was found that the part played by lead was exactly the same as in the case of the copper-antimony alloys. Thus, in the series of alloys in which the tin was the varying element, lead and copper being present in equal quantities, a separation into two alloys took place in every instance until the one with 40 per cent. of tin was reached. No. 4 was the induction-balance curve.

In the second series, that in which the copper varied, the tin and lead bearing a constant ratio to each other, and which had the composition—I.—95 per cent. copper, 2·5 per cent. lead, and 2·5 per cent.

tin; II.—90 per cent. copper, 5 per cent. lead, and 5 per cent. tin; III.—85 per cent., &c., no alloys formed between those with 40 per cent. and 60 per cent. of copper respectively. In the case of the alloys with 44 per cent. of copper, and with 52 per cent. of copper, in which the copper and tin were in approximately the proportions requisite for the formation of the compounds $SnCu_3$ and $SnCu_4$, the turning points of the copper-tin conductivity curve, the separation into two alloys was very marked. The lower alloy consisted for the greater part of the lead originally present in the mixture. No. 5 is the induction-balance curve of this series of alloys.

Owing to the high melting-point of copper it was not found possible to cast the higher members of the series in the mould employed.

As in the case of the copper-antimony alloys, it is evident on comparing the above curve with that of Professor Roberts-Austen, mentioned by Mr. Laurie, that lead is without influence on the character of the copper-tin alloys other than that of a diluent. The influence of the alloys agreeing in composition with the formulæ $SnCu_3$ and $SnCu_4$, is as marked in this series of alloys as those having the compositions represented by $SbCu_2$ and $SbCu_4$ in the copper-antimony series; these four alloys possess physical properties widely different from those of the alloys forming the remainder of their respective series. In connection with this, it is of interest to note that the alloys $SnCu_3$ and $SbCu_2$, the upper turning points in their respective conductivity curves are in the one case blue and in the other purple, these colours being far less apparent in any of the other alloys of the series. Their fracture is crystalline and irregular. The alloys $SnCu_4$ and $SbCu_4$, the lower turning points of the curves, are white in colour, close in texture, and conchoïdal in fracture.

XV.—*On Morindon.*

By T. E. Thorpe, F.R.S., and William J. Smith, M.B. (Lond.).

In a previous communication (Trans., 1887, 52), one of us, in conjunction with Mr. T. H. Greenall, sought to show that, contrary to the supposition of Rochleder and of Stenhouse, morindin, the active colouring matter of A'l, the root-bark of *Morinda citrifolia*, is not identical with ruberythric acid, although both bodies are glucosides, and possess apparently the same percentage composition. That A'l contains substantially the same dyeing principles as madder appears to have been conjectured many years ago, although Anderson, who

first isolated morindin, was unable to satisfy himself of the identity of these substances. Direct evidence that ruberythric acid and morindin are not the same was first adduced by Stein (*J. pr. Chem.*, **97**, 234), who showed that their barium compounds are dissimilar in colour, and that they behave differently towards caustic potash. Moreover, the products obtained on hydrolysing the two substances give different colour reactions, although Stein found that the optical behaviour of solutions of morindon—the product formed on hydrolysing morindin—agreed perfectly with the description given by Stokes, and on which Stenhouse based his assumption that morindon and alizarin were identical.

Part of the obscurity which hangs over the subject is due to the doubt which has existed as to the nature of ruberythric acid. Graebe and Liebermann have, as is well known, suggested that the formula of ruberythric acid is $C_{26}H_{28}O_{14}$, in contradistinction to that of $C_{20}H_{22}O_{11}$, as proposed by Rochleder.

According to Rochleder, the decomposition of ruberythric acid on hydrolysis is represented by the equation—

$$C_{20}H_{22}O_{11} = C_{14}H_8O_4 + C_6H_{12}O_6 + H_2O,$$

which affords 54·8 per cent. of alizarin; whereas according to Graebe and Liebermann it should be—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6,$$

or ruberythric acid should afford 42·5 per cent. alizarin.

It will be noticed that a fundamental difference in the modes of representing the decomposition is that whilst Rochleder's equation requires the separation of water, that of Graebe and Liebermann, in accordance with the generally accepted mode of explaining the process of the hydrolysis of a glucoside, demands its assimilation.

For this reason, we had in the paper referred to adopted Graebe and Liebermann's equation, and we further sought to prove its validity by determining the amount of alizarin yielded by hydrolysing a known weight of some pure ruberythric acid, for which we were indebted to the kindness of Dr. Schunck. This gave 42·1 per cent. of alizarin, in close agreement with the amount demanded by Graebe and Liebermann's equation.

Since the publication of our paper, Liebermann and Bergami (*Ber.*, **20**, 2241) have likewise studied the mode of hydrolysis of ruberythric acid, and they have also analysed the barium salt and an octacetyl compound, with the result that there is no longer any doubt that ruberythric acid has the formula $C_{26}H_{28}O_{14}$.

Ruberythric acid may be regarded as formed by the replacement of

each of the two phenylhydroxyls in alizarin by a grape-sugar rest; thus—

$$C_{14}H_6O_2<\begin{matrix}O\cdot C_6H_7O(OH)_4\\O\cdot CH_7O(OH)_4\end{matrix}.$$

Liebermann and Bergami, who have traced the existence of cane-sugar in madder, have proposed the formula—

$$C_{14}H_6O_2<\begin{matrix}O\cdot C_{12}H_{14}O_3(OH)_7\\OH\end{matrix},$$

which equally well explains all that is known respecting ruberythric acid, and more especially the fact that it is a monobasic acid.

When morindin is heated to a sufficiently high temperature, it chars, and yields a red crystalline sublimate, termed *morindon* by Anderson, its discoverer. This substance, which may more readily be obtained by the hydrolysis of morindin, is, according to Stenhouse, identical with alizarin. In the paper referred to, it was shown that morindon differed from alizarin in certain well-marked colour reactions; the crystalline forms of the two substances were dissimilar, and lastly, their percentage composition was different, that of morindon corresponding to a trihydroxymethylanthraquinone, $C_{15}H_{10}O_5$. The quantity obtained was, however, too small to enable us to do more than determine the percentage composition of the substance and to make a few qualitative reactions.

Mr. Thomas Wardle, of Leek, having placed a quantity of the roots of *M. citrifolia* at our disposal, we have attempted to obtain further evidence of the nature of morindon. The finely powdered root-bark was heated with successive quantities of dilute alcohol (50 per cent.) so long as any colouring matter was dissolved out. The solution was concentrated to half its volume by distillation, and filtered, the filtrate being afterwards subjected to hydrolysis. The precipitate, consisting of morindin and morindon mixed with a large quantity of resin, having been extracted many times, first with benzene, and then with absolute alcohol, in order to remove the morindon, was dissolved by heating with 50 per cent. alcohol. The morindon and morindin were then repeatedly crystallised, the former from benzene, and the latter from dilute alcohol. The total yield from rather less than 4 lbs. of bark was 1·9465 gram of morindin, and 0·3407 gram of morindon.

As the object of the present inquiry was to determine the nature of morindon, all the morindin was converted into morindon by dissolving it in dilute (50 per cent.) alcohol, and heating the solution in a flask attached to a reflux condenser with a small quantity of dilute hydrochloric acid. The operation was made quantitatively, and the yield of morindon determined.

0·4890 gram morindin gave 0·2368 morindon, or 48·4 per cent.
0·9065 „ „ 0·4393 „ 48·4 „

In the former paper we gave the percentage yield of morindon from morindin as 48·5 per cent.

The morindon was then analysed, with the following results:—

(1.) 0·1510 gram gave 0·3683 CO_2 and 0·0534 H_2O.
(2.) 0·1510 „ 0·3682 „ 0·0547 „
(3.) 0·0937 „ 0·2291 „ 0·0327 „

	I.	II.	III.	Calculated for $C_{15}H_{10}O_5$.
C.....	66·52	66·50	66·68	66·66
H.....	3·92	4·02	3·87	3·70
O.....	—	—	—	29·64
				100·00

These analytical numbers agree almost exactly with those given in the first paper.

In order to obtain further insight into the nature of the substance, it was next distilled for us by Dr. Japp with zinc-dust. Only about 0·6 gram was available for this purpose. The product of the distillation was dissolved in hot glacial acetic acid; on cooling, it separated out in lustrous, pale-yellow plates, but the amount was too small to warrant recrystallisation. The once crystallised plates after being dried in the steam oven, melted at 190—191°. This agrees with the melting point (190°) found for *yellow* methylanthracene from coal-tar by Japp and Schultz (*Ber.*, **10**, 1887). Pure (white) methylanthracene melts at 200°.

As the quantity was insufficient for recrystallisation, the crystals were next dissolved in hot glacial acetic acid, and oxidised by chromic acid, the product being treated with solution of sodium carbonate, and precipitated by hydrochloric acid. The gelatinous precipitate, when washed and dried, exhibited the properties of anthraquinonecarboxylic acid. Heated between watch-glasses, it sublimed in slender yellowish needles, melting at 278—280°, indistinguishable in appearance from those of anthraquinone, but soluble in ammonia. The sublimate was recrystallised from hot glacial acetic acid, which deposited it in small yellowish needles with the same melting point as before. When treated with caustic soda solution and zinc-dust, the liquid acquired a yellowish-red colour, which disappeared after exposure to the air. The addition of caustic soda occasioned a precipitate of the sodium salt. These properties agree with those of anthraquinonecarboxylic acid, as described by Liebermann (*Annalen*, **183**, 167).

An attempt was next made to see if phthalic acid could be obtained from morindon. 0·25 gram of the substance was oxidised with permanganate in alkaline solution, but oxalic acid was the only product of oxidation that could be detected. A comparative experiment, in which the same weight of alizarin was oxidised under precisely similar circumstances, yielded phthalic acid, identified by the fluoresceïn reaction.

There appears, therefore, to be no doubt that morindon is not identical with alizarin, but that it is a trihydroxymethylanthraquinone. Up to the present, eight other compounds of the empirical formula $C_{15}H_{10}O_5$ seem to be known, but morindon is not identical with any one of these. It is not possible, with the amount of information which we have as yet, to determine its relations, either to the parent glucoside morindin, or to ruberythric acid.

Since morindin yields 48·4 per cent. of morindon on hydrolysis, it is easy to construct a formula for the former, which shall agree with the quantitative results of the hydrolysis, and at the same time with the empirical composition of morindin as determined by analysis. The formula so got is $C_{26}H_{28}O_{14}$, which expresses the composition of ruberythric acid. But the hydrolysis of a compound containing C_{26} into one containing C_{15} involves the splitting off of an uneven number of carbon-atoms, and this would only be possible if the glucoside contained a sugar like arabinose, that is, one containing 5 atoms of carbon, in addition to a six-carbon sugar. It is at all events certain that the amount of sugar obtained by hydrolysis and as determined by Fehling's solution, did not exceed 35 per cent., on the assumption that the reducing power was the same as that of glucose.

XVI.—*On Manganese Trioxide.*

By T. E. Thorpe, F.R.S., and F. J. Hambly.

The chemical changes attending the action of sulphuric acid upon dry potassium permanganate have been variously described by different observers. It would seem, in the first place, that the nature of the reaction is very considerably modified by the purity of the salt and the strength of the acid. Wöhler (*Annalen*, **86**, 373) observed that when concentrated oil of vitriol was poured over the crystallised salt, the permanganate was decomposed with explosive violence and with the evolution of much heat and even flame, and the formation of a

cloud of finely divided oxide of manganese. Large quantities of oxygen were simultaneously disengaged. Hence Wöhler concluded that free permanganic acid is a gas which at the moment of its liberation is decomposed by the heat of the reaction into oxygen and manganese dioxide. It is not improbable that the phenomena thus described by Wöhler were to some extent caused by the presence of chlorate or perchlorate of potassium in the permanganate. Pure dry potassium permanganate readily and quietly dissolves in the concentrated acid without any very extraordinary rise of temperature. If concentrated sulphuric acid be used, a clear sage-green solution will be obtained. If the monohydrated acid, H_2SO_4,H_2O, is employed, the colour of the solution is dark-brown, and it is seen to contain a number of oily drops which gradually sink, forming a dark reddish-brown liquid which remains fluid at $-20°$. This substance is extremely unstable: on exposure to the air, it slowly evolves oxygen, and the gaseous bubbles as they burst at the surface of the liquid form a violet-coloured cloud. It is highly hygroscopic, and gradually decomposes under the action of the attracted moisture. On dropping it into water, it dissolves with a purple colour, and with the evolution of so much heat that it suffers partial decomposition. Its solution, even when dilute, is gradually but completely resolved on heating into manganese dioxide and oxygen. It dissolves in concentrated sulphuric acid without decomposition, forming the olive-green or sage-green solution before mentioned. It is apparently non-volatile: it may be heated under reduced pressure to about 60° or 65° without the slightest evolution of vapour. At higher temperatures, it is decomposed with a sudden and violent explosion into oxygen and manganese dioxide. The rapidity of the decomposition is probably due to the action of the separated manganese oxide, since Thenard has shown that a minute quantity of this substance when added to the liquid instantly resolves it, even in the cold, into oxygen and manganese dioxide. Silver oxide acts in the same way. It sets fire to paper, and explodes with sulphuretted hydrogen and the vapours of alcohol and ether.

The composition of this body was first correctly ascertained by Aschoff (*Pogg. Ann.*, **3**, 217). On analysis, it gave numbers in exact accordance with the formula of manganese heptoxide, Mn_2O_7.

If potassium permanganate is dropped in small quantities at a time into pyrosulphuric acid, or oil of vitriol to which sulphuric anhydride has been added, as each successive portion of the salt reaches the acid, flames are emitted, together with a cloud of sulphur trioxide, darkened in colour by particles of manganese dioxide. The solution obtained is of a lavender-blue colour, and on standing deposits a pink-coloured salt; this on treatment with cold water

forms a deep brown solution which ultimately deposits brown oxide of manganese.

According to Franke (*J. pr. Chem.*, **14**, 1887), the dark-green solution obtained by the action of concentrated sulphuric acid upon potassium permanganate contains an oxysulphate of manganese of the composition $(MnO_3)_2SO_4$, but no direct evidence for the existence of this compound is adduced by him. The possibility of its existence seems to be mainly based upon the fact that the analogously constituted oxychloride, MnO_3Cl (Aschoff), and oxyfluoride, MnO_3F (Wöhler), are known. The difference between the colours of the solutions obtained by using the concentrated and the monohydrated acids may also be held to indicate differences in the chemical nature of the solutions.*

On cautiously adding a small quantity of water to the well-cooled green solution, manganese heptoxide is obtained. Its formation, according to Franke, may be thus expressed:—

$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$

Hence we may thus explain the production of permanganic anhydride by the use of monohydrated sulphuric acid, and its non-formation when the concentrated acid is employed.

On very cautiously heating the dark-green solution of the permanganate in sulphuric acid in a current of moist air, it gives off small quantities of a violet-coloured body—*apparently* gaseous, which can be condensed in a well-cooled receiver, when it forms a dark-red somewhat viscid mass. This substance was regarded by Terreil as permanganic acid, $HMnO_4$ (*Bull. Soc. Chim.*, 1862, 40), but as it can also be obtained, according to Aschoff, by the gradual decomposition of the heptoxide, it is probably free from hydrogen.

According to Franke this compound is manganese trioxide, MnO_3. Its formation from the green-coloured solution may be expressed as follows:—

$$(MnO_3)_2SO_4 + H_2O = 2MnO_3 + H_2SO_4 + O,$$

and from the heptoxide thus:—

$$Mn_2O_7 = 2MnO_3 + O.$$

All observers agree that its formation is invariably accompanied by the evolution of oxygen, which, according to Schönbein and Böttcher, is strongly ozonised. Subsequent observations have shown that the

* Franke explains the formation of the oxysulphate by the equations—

(1) $2KOMnO_3 + H_2SO_4 = K_2SO_4 + 2OHMnO_3$.
(2) $2OHMnO_3 + H_2SO_4 = (MnO_3)_2SO_4 + 2H_2O$.

oxygen is quite free from ozone, the ozone reactions being caused by the evolved manganese compounds, or probably in certain cases by chlorine or its oxides.

On treating the condensed manganese trioxide with water, it is at once decomposed into manganese dioxide and permanganic acid—

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

Franke, in his first paper (*loc. cit.*) states that the heptoxide is decomposed into manganese dioxide and trioxide, and a *blue* gas giving certain of the reactions of ozone, but differing from that substance in being decomposed at 150° and in being soluble in concentrated sulphuric acid. In a subsequent paper (*loc. cit.*, p. 166), he regards this blue gas, which he also obtained by the action of moist air upon the sulphuric acid solution of potassium permanganate, as *manganese tetroxide*, and represents its formation thus :—

$$(MnO_3)_2SO_4 + H_2O = MnO_4 + MnO_3 + H_2SO_4.$$

According to Franke, the blue gas is best made by passing a stream of carbonic acid gas saturated with moisture on to the surface of the olive-green liquid, and leading the escaping gases through two U-tubes, one of which is empty, and the other filled with calcium chloride. The manganese trioxide condenses in the first tube, whilst the second retains the tetroxide. No analyses of this compound are given. It is said to be more volatile than the trioxide, to be more blue in colour, and to be less readily attacked by water.

A manganiferous gas of a blue colour seemed to be a sufficiently remarkable substance to merit further investigation. We have been led therefore to repeat Franke's experiments, but although we have carefully followed the directions given for its preparation, we have not been so fortunate as to observe the slightest indication of a blue gas, or to obtain any evidence of the existence of manganese tetroxide.

We have, however, succeeded in obtaining manganese trioxide. As our conclusions, however, differ in certain particulars from those of Franke, it may be desirable to describe our experiments in detail.

The first method described by Franke of leading moist carbonic acid gas on to the surface of the solution of potassium permanganate, and collecting the product in empty U-tubes, gave such an extremely small yield of the new oxide, that it seemed hopeless to expect that quantities sufficient even for analysis could be so made. Better results were obtained by the second method. This consists in dropping the acid solution of the permanganate, contained in a tap funnel, on to dry sodium carbonate. As each drop of the solution comes in contact with the carbonate, a slight burst of pink-coloured fume is observed,

which is mechanically carried forward in the current of carbonic acid. After a time the evolution of the coloured fume ceases, but on attaching a fresh flask containing sodium carbonate it can be renewed—

$$(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + O.$$

In order to collect the oxide, the evolved products were passed through a small U-tube filled with fragments of broken glass and immersed in a mixture of ice and salt. If the broken glass be omitted, the greater portion of the pink fume passes through the apparatus along with the carbonic acid. The freezing mixture is necessary to retard the decomposition of the condensed product, since at ordinary temperatures it gradually loses oxygen, and is converted into manganese dioxide. The curious behaviour of the pink fume has led us to conclude that it is really an extremely finely-divided solid. It floats in the air like a cloud of sal-ammoniac or sulphur trioxide, and like these substances may, if suspended in a sufficiently large volume of air or carbonic acid, be passed through water practically unabsorbed.

The U-tube containing the broken glass was connected with a second U-tube containing dilute sulphuric acid, and immersed in ice-cold water. The flask containing the sodium carbonate was also surrounded by cold water in order to moderate the intensity of the action, and prevent as far as possible rise of temperature. This form of apparatus was adopted after a number of trials with other arrangements, as it was found to be best adapted to the plan of analysis which we employed in order to ascertain the composition of the condensed product.

The amount of the oxide obtained even from a well-conducted operation is so very small that the ordinary gravimetric methods for the estimation of manganese are difficult of application. If large quantities of the strongly acid solution be allowed to come in contact with the carbonate at a time, the local heating is so great that the product is liable to be contaminated with manganese dioxide; on the other hand, if the operation be unduly prolonged, the same oxide is apt to be formed by the gradual decomposition of the trioxide. Fortunately we have in Chatard's process a volumetric method of estimating even minute quantities of manganese with a high degree of accuracy. This method consists in boiling the solution containing the manganese compound, which should be free from chlorine, with nitric acid and lead dioxide, and determining the amount of permanganate formed by means of a decinormal solution of ammonium oxalate. A preliminary examination of this method enabled us to determine the conditions under which it was applicable to the present case (see p. 182).

The details of one of the experiments in which the trioxide was prepared and analysed will serve to show the mode in which the operations were carried out.

Six grams of potassium permanganate, free from perchlorate, were dissolved in 100 c.c. of concentrated sulphuric acid, and the solution allowed to drop from a tap-funnel on to dry sodium carbonate contained in a distilling flask. The carbonic acid carrying with it the oxide of manganese was first passed through a U-tube filled with fragments of glass and immersed in a mixture of ice and salt; the oxide of manganese which escaped condensation then passed through 20 c.c. dilute sulphuric acid contained in a bulbed U-tube. The product in the first U-tube was then treated with water, the solution filtered through glass wool and titrated with ammonium oxalate (1 c.c. = 0·0088 O or 0·001558 MnO). The solution required 11·5 c.c. of the oxalate solution for decolorisation. On reoxidation with nitric acid and lead oxide, it needed 11·4 c.c.

Available oxygen	0·01012
MnO	0·01776
MnO_x	0·02788

$$0{\cdot}01776\ \text{MnO} = 0{\cdot}01375\ \text{Mn}.$$

$$\text{Per cent. Mn} = \frac{0{\cdot}01375 \times 100}{0{\cdot}02788} = 49{\cdot}3.$$

$$\text{Per cent. O} = \frac{0{\cdot}01413 \times 100}{0{\cdot}02788} = 50{\cdot}7.$$

The acid solution decanted from the bulbed U-tube was titrated with the standard ammonium oxalate, of which it required 4·8 c.c. for decolorisation. After reoxidation by lead dioxide and nitric acid, 6·15 c.c. were required—

Available oxygen	= 0·00088 × 4·8 = 0·00422
MnO	= 0·001558 × 6·15 = 0·00958

$$0{\cdot}00958\ \text{MnO} = 0{\cdot}00742\ \text{Mn}.$$

$$\text{Per cent. Mn} = \frac{0{\cdot}00742 \times 100}{0{\cdot}0138} = 53{\cdot}8.$$

$$\text{Per cent. O} = \frac{0{\cdot}00638 \times 100}{0{\cdot}0138} = 46{\cdot}2.$$

The results of the various analyses made in this way are seen in the following table :—

	In aqueous solution.		In acid solution.	
	P. c. Mn.	P. c. O.	P. c. Mn.	P. c. O.
Experiment I	49·3	50·7	not determined	
„ II	49·1	50·9	53·9	46·1
„ III	48·8	51·2	not determined	
„ IV	49·3	50·7	53·8	46·2
„ V	49·6	50·4	53·1	46·9
„ VI	49·0	51·0	52·8	47·2
„ VII	49·3	50·7	52·5	47·5
„ VIII	49·3	50·7	52·7	47·3
„ IX	49·4	50·6	52·9	47·1
„ X	not determined		52·5	47·5*

Means—

Aqueous Solution.

	Found.	Mn_2O_7 calculated.
Mn	49·25	49·46
O	50·74	50·54
	99·99	100·00

Acid Solution.

	Found.	MnO_3 calculated.
Mn	53·03	53·31
O	46·97	46·69
	100·00	100·00

From these results, it appears that when a solution of potassium permanganate in concentrated sulphuric acid is dropped on to dry sodium carbonate, manganese trioxide is formed in very small quantities as a reddish-pink cloud. The finely-divided powder is deposited upon the smaller glass tubes of the apparatus as a reddish, amorphous, deliquescent mass. The substance appears to be fairly stable when kept in a freezing mixture, but at ordinary temperatures it slowly decomposes. As obtained in a U-tube kept in a freezing mixture, it has upon the sides of the tubes a reddish-pink colour by transmitted light, but at the bottom of the tube where the greater part collects, the colour by reflected light is almost black. Treated with water, it is decomposed in accordance with the equation—

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

* Vapour passed directly into the acid, *i.e.*, without intermediate U-tube.

The validity of this equation was experimentally verified. The manganese dioxide obtained on treating the product formed in Experiment VIII with water was determined: the ratio of its amount to that in solution as permanganic acid was exactly as 1 to 2.

When the substance is absorbed by dilute sulphuric acid, a clear pink or reddish-pink solution is obtained, in which the manganese and oxygen are in the ratio of 1 to 3. There is no evidence to show that this solution contains free manganic acid. If the substance were decomposed as in the aqueous solution, the ratio of O to Mn would be as 1 to 3, provided that all the manganese were retained in solution.

When manganese trioxide is dissolved in concentrated sulphuric acid, it forms a solution of the same colour as that obtained on dissolving potassium permanganate in oil of vitriol. This may be regarded as additional evidence for the existence of $(MnO_3)_2SO_4$. The substance is soluble in caustic potash, and gives a green solution similar to that of potassium manganate.

Manganese trioxide gives the reactions for ozone: it affects mercury and liberates iodine from potassium iodide. It blackens silver, but the stain can be shown to be due to manganese dioxide.

There is no proof that ozone is liberated by the action of oil of vitriol upon pure potassium permanganate.

XVII.—*Note on Chatard's Method for the Estimation of Small Quantities of Manganese.*

By T. E. Thorpe, F.R.S., and F. J. Hambly.

Chatard's method for the estimation of small quantities of manganese is based on Crum's qualitative reaction, and consists in boiling the manganese solution, which must be free from chlorine, with lead peroxide and nitric acid, filtering the liquid through asbestos from the excess of lead peroxide, and titrating the permanganic acid formed with a standard solution of ammonium oxalate. Chatard states that his method is only applicable when small quantities of manganese are present, although no experimental evidence is given as to the limits within which the process is available; he simply obtained concordant results in the estimation of the small quantities of manganese in limestones and dolomites (*American Journal of Science and Arts*, **50**).

The final point in the titration with ammonium oxalate is apt to be

obscured by the precipitation of lead carbonate, and in order to obviate this inconvenience, Leclerc (*Compt. rend.*, **75**, 1209) has proposed to use a solution of mercurous nitrate in excess of nitric acid, instead of ammonium oxalate, the final point in the reaction being a transition in colour from reddish to greenish-yellow.

By a slight modification of the original process, the precipitation of the carbonate may be obviated. If the oxidation of the manganese by means of lead peroxide and nitric acid is made in presence of sulphuric acid, no lead passes into solution, and the filtered liquid remains perfectly clear on titration with ammonium oxalate.

To ascertain within what limits the method is trustworthy, and also to determine the most favourable conditions for complete oxidation of the manganese, a solution of manganous sulphate was prepared containing 1 mgrm. of manganese per c.c. with which estimations were made by boiling for different times varying proportions of manganese, nitric acid and sulphuric acid. A solution of ammonium oxalate of about decinormal strength, standardised against weighed quantities of potassium permanganate, was used for the titrations. The method works well with weights of manganese from 0·004—0·008 gram; it is not to be depended on when more than 0·01 gram is present, with 0·01 gram in solution, the results were generally 0·0004 gram too low. Care must of course be taken to prevent the presence of any possible reducing agents, and it was found advisable to always wash down the sides of the flask in which the oxidation was being performed, about half a minute before the boiling was stopped. The following is the method finally adopted:—To the manganese solution, which must be free from chlorine and not too dilute, say about 25 c.c., add 5 c.c. concentrated nitric acid, 2—3 grams of lead peroxide, and from 10—20 c.c. of dilute sulphuric acid (1 part of acid to 2 of water). Boil gently for about four minutes, wash down the sides of the flask with hot water, and continue the boiling for half a minute longer. Allow the lead sulphate and excess of peroxide to subside, and filter at once, by the aid of a filter-pump, through a plug of asbestos previously ignited and washed with dilute sulphuric acid. Wash the residue in the flask with boiling water by decantation, heat the clear filtrate to 60°, and titrate with ammonium oxalate.

The following results were obtained in estimations of known quantities of manganese:—

Mn taken.		Mn found.
0·005	.....	0·0051 0·0049 0·0049
0·006	.....	0·0060 0·0060

Mn taken.		Mn found.
0·007	.....	0·0069
0·008	.....	0·0081
0·009	.....	0·0091
0·01	.....	0·0097 0·0096 0·0096

XVIII.—*Action of Phenylhydrazine on an Unsaturated γ-Diketone.*

By Francis R. Japp, F.R.S., and G. N. Huntly.

The saturated γ-diketones, such as acetonyl-acetone, are known to react with 2 mols. of phenylhydrazine to form colourless dihydrazides.

In studying the behaviour of an unsaturated γ-diketone—anhydracetophenonebenzil—with phenylhydrazine, we have obtained a different result. The reaction occurs according to the equation—

$$\begin{matrix} C_6H_5\cdot C : CH\cdot CO\cdot C_6H_5 \\ | \\ C_6H_5\cdot CO \end{matrix} + C_6H_5\cdot NH\cdot NH_2 = C_{28}H_{22}N_2 + H_2O + O,$$

the reduction involved in the process being probably effected at the expense of a second molecule of phenylhydrazine.

52 grams of anhydracetophenonebenzil and 36 grams of phenylhydrazine were mixed with alcohol and heated in a soda-water bottle at 100° for three and a half hours. At the end of this time, the new compound had separated in the form of a heavy, canary-yellow, crystalline powder, consisting of short needles, which, as the liquid cooled, became mixed with a large quantity of oily matter. There was considerable escape of gas on opening the bottle. The oily matter was readily removed by washing with ether, in which the crystalline substance is practically insoluble. The yellow needles were seen to be contaminated with a small quantity of a white crystalline substance, but it was found that this also could be removed by further washing with ether. After this treatment, the compound appeared quite homogeneous; but since, owing to its sparing solubility in all the ordinary organic menstrua, it could not be readily recrystallised, it was, as a further precaution, boiled with a considerable volume of alcohol, after which it was dried at 100° and in this condition

analysed. It melted, with blackening and decomposition, at 231—232°. The yield from the above quantities was only 14 grams.

	Substance.	CO_2.	H_2O.
I.....	0·2542	0·8107	0·1344
II.....	0·1858	0·5921	0·0954

III. 0·1263 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18°, and under 451 mm. pressure. After absorption of the nitric oxide, there remained 13·79 c.c. of dry nitrogen at 18° and under 423 mm. pressure.

	Calculated for $C_{28}H_{22}N_2$.		Found.		
			I.	II.	III.
C_{28}.....	336	87·0	87·0	86·9	—
H_{22}.....	22	5·7	5·9	5·7	—
N_2	28	7·3	—	—	7·4
	386	100·0			

A different preparation gave similar figures.

A condensation such as the foregoing would in all probability lead to the formation of a closed-chain compound, possibly with two nitrogen-atoms in the ring. We intend to study the reactions of the substance with the view of throwing light on its constitution. We hope, further, to prepare analogous compounds from other unsaturated γ-diketones.

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XIX.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE OWENS COLLEGE.

The Synthetical Formation of Closed Carbon-chains. Part III (*continued*). *Some Derivatives of Pentamethylene.*

By H. G. Colman, B.Sc., and W. H. Perkin, Junr., Ph.D.

In a paper on Pentamethylene-derivatives communicated to the Society by one of us some time since, it was shown that a synthesis of a 5-carbon chain could be easily brought about by the following simple reactions:—If the sodium compound of ethylic malonate be

treated with trimethylene bromide, ethylic tetramethylenedicarboxylate and ethylic pentane-ω_2-ω_3-tetracarboxylate are formed, the latter being produced according to the following reaction:—

$$2CHNa(COOC_2H_5)_2 + BrCH_2\cdot CH_2\cdot CH_2Br = (COOC_2H_5)_2CH\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + 2NaBr.$$

Ethylic pentane-ω_2-ω_3-tetracarboxylate.

If ethylic pentanetetracarboxylate is mixed with sodic ethylate, it yields a disodium-derivative, and this when treated with bromine or iodine yields ethylic pentamethylenetetracarboxylate, thus:—

$$(COOC_2H_5)_2CNa\cdot[CH_2]_3\cdot CNa(COOC_2H_5)_2 + Br_2 = \begin{matrix} & CH_2—C(COOC_2H_5)_2 \\ CH_2 & \quad\quad\quad | \\ & CH_2—C(COOC_2H_5)_2 \end{matrix} + 2NaBr.$$

Ethylic pentamethylenetetracarboxylate.

This method for the preparation of the 5-carbon chain differs widely from that employed in the case of the tetramethylene-derivatives (Trans., **51**, 1), but it was resorted to because it was at the time found impossible to prepare a bromide of the formula $BrCH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$ which when treated with the sodium compound of ethylic malonate should have yielded pentamethylene-derivatives directly, thus:—

$$2CHNa(COOC_2H_5)_2 + BrCH_2\cdot CH_2\cdot CH_2\cdot CH_2Br = \begin{matrix} & CH_2—CH_2 \\ CH_2 & \quad\quad | \\ & CH_2—C(COOC_2H_5)_2 \end{matrix} + CH_2(COOC_2H_5)_2 + 2NaBr.$$

Ethylic pentamethylenedicarboxylate (1, 1).

This difficulty has, however, since to some extent been overcome.

In a paper brought before the Society last November (Trans., **51**, 820), Freer and Perkin showed that acetyltrimethylenecarboxylic acid when boiled with water was split up into acetopropyl alcohol and carbonic anhydride, thus:—

$$\begin{matrix} CH_3\cdot CO \\ COOH \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + H_2O = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2OH + CO_2.$$

Acetopropyl alcohol.

This ketone alcohol when subjected to the action of sodium amalgam is easily converted into γ-pentylene glycol (*loc. cit.*, p. 836) thus:—

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2OH + H_2 = CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2OH,$$

γ-Pentylene glycol.

and thus glycol, on heating with concentrated aqueous hydrogen bromide, yields methyltetramethylene dibromide according to the following equation :—

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH + 2HBr = CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + 2H_2O.$$

Methyltetramethylene dibromide.

On treating this dibromide with the sodium compound of ethylic malonate, it was found that decomposition took place very easily, with formation of ethylic methylpentamethylenedicarboxylate (2, 1, 1), thus :—

$$2CHNa(COOC_2H_5)_2 + CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = \begin{matrix} CH_2 & \begin{matrix} CH_2{-}CH{\cdot}CH_3 \\ | \\ CH_2{-}C(COOC_2H_5)_2 \end{matrix} \end{matrix} + CH_2(COOC_2H_5)_2 + 2NaBr.$$

Ethylic methylpentamethylene-dicarboxylate (2, 1, 1).

This ethereal salt, on hydrolysis, yields the free dicarboxylic acid which, when heated a few degrees above its melting point, is decomposed into carbonic anhydride and methylpentamethylenemonocarboxylic acid :—

$$\begin{matrix} CH_2 & \begin{matrix} CH_2{-}CH{\cdot}CH_3 \\ | \\ CH_2{-}C(COOH)_2 \end{matrix} \end{matrix} = \begin{matrix} CH_2 & \begin{matrix} CH_2{-}CH{\cdot}CH_3 \\ | \\ CH_2{-}CH{\cdot}COOH \end{matrix} \end{matrix} + CO_2.$$

Methyl pentamethylenemono-carboxylic acid (2, 1).

While carrying on these experiments, it was thought that the study of the action of methyltetramethylene dibromide on the sodium compound of ethylic acetoacetate would be likely to give interesting results, and it is therefore included in this paper.

In papers on the action of trimethylene bromide on the sodium compounds of ethylic malonate and ethylic acetoacetate (Trans., **51**, 1 and 702), it was shown that the two compounds, which are usually so analogous in their reactions, in this case gave rise to compounds entirely differently constituted. Thus when ethylic malonate is used, ethylic tetramethylenedicarboxylate, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C(COOC_2H_5)_2$, is formed; whereas in the case of ethylic acetoacetate a curiously constituted compound—

$$\begin{matrix} CH_3{\cdot}C{-}O{-}CH_2 \\ \| \quad\quad | \\ COOC_2H_5{\cdot}C{-}CH_2{-}CH_2 \end{matrix}$$

(ethylic methyldehydrohexonecarboxylate) is produced. From these experiments it seemed probable that on treating ethylic acetoacetate with methyltetramethylene dibromide, a similarly constituted ethylic dimethylheptonecarboxylate would be formed, according to the equation—

$$2CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2Br = \begin{matrix} CH_3\cdot C(-O-CH_2-CH_2-)\\ COOC_2H_5\cdot CH\cdot CH(CH_3)\cdot CH_2 \end{matrix} + CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + 2NaBr.$$

Ethylic dimethylheptonecarboxylate [2, 4, 3].

On studying this decomposition, however, it was soon found that this was not the case, the reaction with ethylic acetoacetate taking place in a way exactly similar to that described above with methyltetramethylene dibromide and ethylic malonate, ethylic acetylmethylpentamethylenecarboxylate being produced, thus:—

$$2CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2Br = \begin{matrix} CH_2 & CH_2-CH\cdot CH_3\\ & \\ CH_2 & CH_2-C(CO\cdot CH_3)\cdot COOC_2H_5 \end{matrix} + CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + 2NaBr.$$

Ethylic acetylmethylpentamethylenecarboxylate [1, 2, 1].

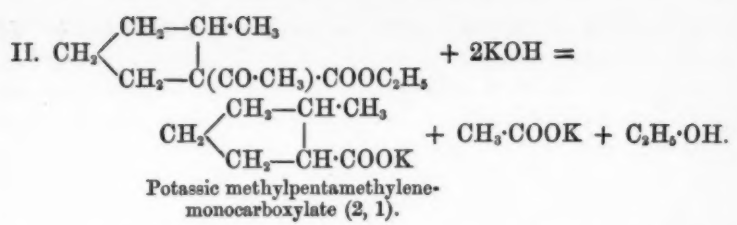
That this is really the constitution of this substance is easily proved from the study of the products obtained from it by hydrolysis with alcoholic potash. When boiled with a strong solution of alcoholic potash for some hours, this ethereal salt is completely split up with formation of methylpentamethylene methyl ketone, methylpentamethylenecarboxylic acid, and other products.

This hydrolysis takes place—as in all cases when substituted ethylic acetoacetates are treated with alcoholic potash—in two distinct phases:—

I. $$\begin{matrix} CH_2 & CH_2-CH\cdot CH_3\\ & \\ CH_2 & CH_2-C(CO\cdot CH_3)\cdot COOC_2H_5 \end{matrix} + 2KOH =$$

$$\begin{matrix} CH_2 & CH_2-CH\cdot CH_3\\ & \\ CH_2 & CH_2-CH\cdot CO\cdot CH_3 \end{matrix} + C_2H_5\cdot OH + K_2CO_3.$$

Methylpentamethylene methyl ketone (2, 1).



Potassic methylpentamethylene-monocarboxylate (2, 1).

The methylpentamethylenemonocarboxylic acid obtained thus was found to be identical with that prepared by the decomposition of methylpentamethylenedicarboxylic acid. Had the reaction between ethylic acetoacetate and methyltetramethylene dibromide taken place as indicated above, with formation of ethylic dimethylheptonecarboxylate, this ethereal salt on hydrolysis should have simply yielded the free acid, without any decomposition-products. (See Methyldehydrohexoncarboxylic acid, Trans., **51**, 715.)

Constitution of Acetopropyl Alcohol.

In their description of acetopropyl alcohol (Trans., **51**, 830), Freer and Perkin show that from a study of the method of preparation as well as from the numbers obtained as the magnetic rotation of this compound, that it evidently has the constitution—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH.$$

Before starting these experiments, however, with methyltetramethylene dibromide, it was thought that it would be more satisfactory to obtain some further proof of the constitution of this important substance, as of course otherwise no definite conclusions could be formed as to the nature of the rings synthesised in the subsequent reactions. Fortunately this can easily be done in the following way:—If acetopropyl alcohol has really the constitution given above, it must evidently, on oxidation, yield levulinic acid, thus:—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH + O_2 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + H_2O.$$

On making the experiment, this was found to be the case.

In carrying out this oxidation, 30 grams of acetopropyl alcohol were dissolved in 100 grams of water, and then the calculated quantity of chromic acid and sufficient dilute sulphuric acid very slowly added, the mixture being cooled with ice during the operation. The reaction was very violent, the chromic acid on coming into contact with the acetopropyl alcohol being instantly reduced.

When the oxidation was finished, the product, which smelt strongly of acetic acid, was extracted at least 10 times with pure ether, the ethereal solution dried over calcic chloride, the ether distilled off, and

the residual oil fractioned under reduced pressure (150 mm.). At first a considerable quantity of acetic acid distilled over (produced by the further oxidation of levulinic acid), then the thermometer rose rapidly to 180°, between which temperature and 215° nearly the whole passed over as a thick, slightly yellowish oil. This on refractioning boiled for the most part between 197° and 203° (150 mm.), and gave the following numbers on analysis, which agree with those required for levulinic acid:—

0·2501 gram substance gave 0·1552 gram H_2O and 0·4790 gram CO_2.

	Theory. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.	Found.
C	51·72 per cent.	52·25 per cent.
H	6·89 „	6·89 „
O	41·38 „	40·86 „

In order to be certain of the constitution of this acid, the silver salt was prepared and analysed.

For this purpose, the fraction 197—203° was dissolved in a little water, carefully neutralised with ammonia, and excess of nitrate of silver added. The white amorphous silver salt thus precipitated was collected, washed, and dissolved in a little hot water. This solution on cooling deposited the silver salt as a colourless mass, which consisted of small colourless nodules. Unfortunately, the characteristic crystals of this salt could not be obtained, owing to the smallness of the quantity at our disposal.

An analysis which was made with a portion dried over sulphuric acid in a vacuum left no doubt, however, as to the constitution of the salt.

0·2274 gram substance gave 0·2247 gram CO_2, 0·0711 gram H_2O, and 0·1106 gram Ag.

	Theory. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOAg$.	Found.
C	26·90 per cent.	26·94 per cent.
H	3·14 „	3·47 „
Ag	48·43 „	48·63 „

Acetopropyl alcohol, prepared by boiling acetyltrimethylenecarboxylic acid with water, has therefore the constitution—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH.$$

Methyltetramethylene Dibromide, $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.

This dibromide is best prepared in the following way:—50 grams of acetyltrimethylenecarboxylic acid (prepared according to the

method given by Freer and Perkin, Trans., **51**, 829) are mixed with about 150 c.c. of water, and boiled for 14 to 20 hours in a flask connected with a reflux condenser. In doing this, it has been found convenient to connect the end of the condenser with a glass tube, dipping into a cylinder 200—300 mm. long filled with mercury, as by this means not only the temperature of the boiling water is raised and the decomposition thus hastened, but also by observing the rapidity of the evolution of the carbonic anhydride it is easy to see how the reaction is progressing and when it is finished. The solution of acetopropyl alcohol thus obtained is poured out into a flat porcelain dish and mixed with about 800 grams of 3 per cent. sodium amalgam. The amalgam must be added very slowly, and the reduction should take from two to three days.

In isolating the product of this reaction, some difficulty was experienced, as γ-pentylene glycol is so readily soluble in water, that even after extracting its solution 20 to 30 times with ether only about half of the amount present is obtained. In order to avoid this loss, the following method was devised :—

The solution containing the glycol and the caustic soda formed during the reduction is separated from the mercury by means of a separating funnel, thoroughly saturated with carbonic anhydride, mixed with about 10 times its volume of absolute alcohol (or purified methylated spirit), and allowed to stand in a cool place for about 24 hours. By this means, nearly all the carbonate of soda is precipitated on the bottom and sides of the vessel containing the solution as a hard crust, whilst the whole of the γ-pentylene glycol remains in the supernatant liquid ; this is poured off and filtered. In order to avoid loss, the cake of carbonate of soda is broken up, well washed on a vacuum pump with absolute alcohol, and the combined alcoholic solutions very carefully fractioned with a long colonna. This precaution is very necessary, as γ-pentylene glycol is very easily carried over with the vapours of alcohol or water, and serious loss occurs if the alcohol is distilled off in the ordinary way.

The distillation is carried on until the thermometer stands at 95°, the residue then consisting of an aqueous solution of γ-pentylene glycol, in which a small quantity of carbonate of soda is dissolved. From this solution methyltetramethylene dibromide is prepared, by connecting the flask containing it with a reflux condenser, and then saturating with hydrogen bromide, the stream of gas being led in rapidly enough to raise the temperature of the liquid to the boiling point. The flask is then placed in a paraffin bath, vigorously boiled for about half an hour, a stream of hydrogen bromide being passed through all the time. When the product is cool, it is mixed with a little water and extracted four or five times with ether. The ethereal

solution is washed with water, dried over calcic chloride, and the ether distilled off, when the crude methyltetramethylene dibromide remains behind as a dark-coloured heavy liquid. On fractioning under reduced pressure (150 mm.), nearly the whole of this crude product passes over between 143° and 150°, and on repeatedly fractioning a beautifully colourless liquid is obtained boiling constantly at 145—147° (150 mm.).

A little hydrogen bromide is always given off during distillation, and to this the slight deficiency in bromine found on analysis is due.

Analysis.

0·2010 gram substance gave 0·3245 gram AgBr.

Theory. $C_5H_{10}Br_2$.	Found.
69·56 per cent.	68·65 per cent.

Methyltetramethylene dibromide is a heavy colourless oil possessing a powerful and unpleasant odour, resembling to some extent that of trimethylene bromide. On exposure to air and light, it gradually becomes dark coloured.

Ethylic Methylpentamethylenedicarboxylate, $CH_2\begin{cases}CH_2—CH\cdot CH_3\\ \quad\quad\quad\quad\quad|\\ CH_2—C(COOC_2H_5)_2\end{cases}$.

To prepare this ethereal salt, 13 grams of sodium was dissolved in 130 grams of absolute alcohol, and to this solution a mixture of 91 grams of ethylic malonate and 65 grams methyltetramethylene dibromide was added, care being taken to keep the whole well cooled during the mixing. When this mixture was warmed on a water-bath, a brisk reaction set in, sodium bromide separated, and it is probable that as soon as this ceased the decomposition was complete. The product was, however, as a precaution, gently boiled on a water-bath for two hours, and then tested with litmus-paper in the usual way, when it was found to have a perfectly neutral reaction.

After distilling off the excess of alcohol and adding water, an oil was precipitated, which was separated from the aqueous solution by extraction with ether, the ethereal solution well washed with water, dried over calcic chloride, and the ether distilled off. In this way an almost colourless oil was obtained, which was purified by fractional distillation. As soon as the last traces of ether had distilled over, the temperature rose rapidly to 190°, and the whole distilled over below 250°, leaving only a trace of residue.

This distillate, on several times refractioning, was easily separated into two parts, one boiling at 190—195°, and consisting of regenerated

ethyl malonate, and a higher fraction boiling constantly at 243—244°, which was pure ethylic methylpentamethylenedicarboxylate.

Analysis.

0·1911 gram substance gave 0·1500 gram H_2O and 0·4437 gram CO_2.

	Theory. $C_{12}H_{20}O_4$.	Found.
C	63·15 per cent.	63·32 per cent.
H	8·77 „	8·73 „
O	28·07 „	27·95 „

Ethylic methylpentamethylenedicarboxylate is a thick, colourless oil of peculiar odour, somewhat resembling that of ethylic tetramethylenedicarboxylate.

The yield of this ethereal salt obtained in the above reaction is almost quantitative.

Methylpentamethylenedicarboxylic Acid, $CH_2\begin{cases}CH_2—CH\cdot CH_3\\ \quad\quad\quad\quad|\\ CH_2—C(COOH)_2\end{cases}$.

This acid is easily prepared from its ethylic salt by hydrolysis with alcoholic potash.

For this purpose, the fraction of ethylic methylpentamethylenedicarboxylate boiling at 240—250° is mixed with one and a half times the calculated quantity of potash, dissolved in pure alcohol, and the whole boiled in a reflux apparatus for 6—8 hours. If at the end of this time a sample taken out and diluted with water is found to dissolve completely without the separation of oily particles, the hydrolysis is complete, otherwise the boiling must be continued until this result is obtained. The alcohol is now distilled off, the residue dissolved in water, and evaporated gently on a water-bath until the last traces of alcohol have been driven off.

The resulting almost colourless liquid is well cooled, acidified with dilute sulphuric acid, and extracted several times with ether. After carefully drying over calcic chloride and distilling off the ether, the crude acid is obtained as a colourless crystalline cake. This is first roughly separated from traces of mother-liquor, by spreading out on a porous plate, and then purified by recrystallisation from ether. It is thus obtained in the form of magnificent colourless prisms, which, after drying over sulphuric acid in a vacuum, gave the following numbers on analysis :—

0·1815 gram substance gave 0·3720 gram CO_2 and 0·1157 gram H_2O.

	Theory. $C_6H_{10}(COOH)_2$.	Found.
C	55·81 per cent.	55·88 per cent.
H	6·97 „	7·08 „
O	37·21 „	37·04 „

Methylpentamethylenedicarboxylic acid melts at 173—175°, decomposing at the same time into carbonic anhydride and methylpentamethylenemonocarboxylic acid.

It is readily soluble in alcohol, ether, and hot water, much more sparingly so in cold water. It crystallises from its solution in hot water, in curious, opaque, leaf-like crystals, but the best crystals are obtained from ether. If the concentrated ethereal solution is allowed to evaporate spontaneously, magnificent transparent prisms form on the sides and bottom of the vessel containing it. These are being crystallographically examined, and we hope shortly to be able to communicate to the Society the crystalline form and measurements of these beautiful crystals.

The *silver* salt of methylpentamethylenedicarboxylic acid was prepared in the usual way by adding an excess of nitrate of silver to the neutral solution of the ammonium salt. The white precipitate thus obtained was well washed with water, dried over sulphuric acid in a vacuum, and analysed.

I. 0·2888 gram of substance gave 0·2594 gram CO_2 and 0·0676 gram H_2O.

II. 0·2817 gram of substance gave 0·1574 gram Ag.

	Theory. $C_6H_{10}(COOAg)_2$.	Found.
C	24·87 per cent.	25·01 per cent.
H	2·59 „	2·66 „
O	55·96 „	55·88 „

Methylpentamethylenemonocarboxylic Acid, $CH_2\begin{cases}CH_2—CH\cdot CH_3\\ \quad\quad\quad\quad\quad|\\ CH_2—CH\cdot COOH\end{cases}$.

When methylpentamethylenedicarboxylic acid is heated a few degrees above its melting point, it is rapidly decomposed into carbonic anhydride and methylpentamethylenemonocarboxylic acid. In carrying out this decomposition, the pure dicarboxylic acid was placed in a small Würtz flask, and gently heated in a metal bath, till the evolution of carbonic anhydride ceased. The residual oily monocarboxylic acid, on fractioning, distilled over completely between 218° and 220°, and on refractioning, the substance was easily obtained pure as a colourless liquid, boiling constantly at 219·5—220·5°.

Analysis.

0·1973 gram substance gave 0·4760 gram CO_2 and 0·1682 gram H_2O.

	Theory. $C_6H_{11}(COOH)$.	Found.
C	65·62 per cent.	65·73 per cent.
H	9·38 „	9·46 „
O	25·00 „	24·81 „

Methylpentamethylenemonocarboxylic acid is a thick, colourless oil of penetrating and most unpleasant odour, somewhat resembling that of valerianic acid. It is not acted on by bromine in the cold, but when heated with bromine at 110° decomposition takes place with evolution of large quantities of hydrogen bromide, showing that the acid is a saturated compound. In order to prove this still more conclusively, a very pure sample was prepared, boiling constantly at 219—219·5°, and submitted to physical examination by W. H. Perkin, sen. The determinations of its specific gravity and magnetic rotation gave the following numbers:—

$$d\frac{15°}{15°} = 1·02054,$$

$$d\frac{20°}{20°} = 1·01739,$$

$$d\frac{25°}{25°} = 1·01438.$$

Magnetic Rotation.

	t.	Sp. rotation.	Mol. rotation.
	24·5°	0·9864	6·898
	24·0	0·9853	6·905
	24·0	0·9897	6·935
	24·0	0·9877	6·920
Average	24·1	0·9873	6·914

In discussing the formation of tetramethylene-derivatives from ethylic malonate and trimethylene bromide (Trans., **51**, 14—17), it was pointed out that by this reaction either tetramethylene or allyl derivatives might be formed.

Thus the monocarboxylic acid obtained by the hydrolysis of the product of this reaction and subsequent elimination of carbonic anhydride might be either—

(*a*.) Tetramethylenecarboxylic acid: $\begin{matrix} CH_2—CH_2 \\ | \quad\quad | \\ CH_2—CH_2\cdot COOH \end{matrix}$

or

(*b*.) Allylacetic acid: $CH_2 : CH\cdot CH_2\cdot CH_2\cdot COOH$.

That the substance actually obtained was not allylacetic acid was easily proved by direct comparison with this well-known acid. In doing this, perhaps the most striking proof of the remarkable difference existing between these two acids was the study of the numbers representing the magnetic rotation of each. Thus:—

Magnetic rotation of	allylacetic acid....	6·426
,, ,,	tetramethylenecarboxylic acid.....	5·048
	Difference....	1·378

Now, unless some decisive proof is brought to the contrary, exactly the same argument might be used with regard to the constitution of the products obtained by the action of methyltetramethylene dibromide on ethylic malonate.

The substance described as ethylic methylpentamethylenedicarboxylate might be an unsaturated compound, having one of the following formulæ:—

(1.) $(COOC_2H_5)_2CH\cdot CH(CH_3)\cdot CH_2\cdot CH : CH_2$.
(2.) $(COOC_2H_5)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH : CH_2$.

in which case methylpentamethylenemonocarboxylic acid would be either—

(A.) $COOH\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH : CH_2$.
(B.) $COOH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH : CH_2$.

Now an acid represented by Formula B is nothing more than allylacetic acid, $COOH\cdot CH_2\cdot CH_2\cdot CH : CH_2$, plus $2CH_2$. Its magnetic rotation is therefore easily calculated, thus:—

Magnetic rotation of allylacetic acid	6·426
$+ 2CH_2 = 2 \times 1·023$.....	2·046
Calc. rotation for acid B	8·472

An acid of the constitution represented by Formula A would have a still higher magnetic rotation (see W. H. Perkin, sen., Trans., **45**, 551), probably about 8·590.

The difference between these two numbers, 8·472 and 8·590, and that actually found (6·914) is very remarkable, and shows conclusively that the acid described as methylpentamethylenecarboxylic acid cannot

possibly be an unsaturated substance, but is really a pentamethylene-derivative.

Methylpentamethylenemonocarboxylic acid is a feeble acid. It dissolves but slowly in dilute ammonia, and if this solution is allowed to stand for some days over sulphuric acid in a vacuum, the ammonium salt is completely decomposed into ammonia and the free acid which separates out in large oily drops. In preparing the *silver* salt, the acid was dissolved in ammonia, neutralised with dilute nitric acid, and a small quantity of the silver salt precipitated. This was filtered off and discarded. The filtrate was then mixed with an excess of nitrate of silver, the white amorphous precipitate thus obtained collected, well washed with water, and dried on a piece of porous plate over sulphuric acid in a vacuum.

Analyses.

I. 0·2847 gram substance gave 0·1305 gram silver.
II. 0·2816 „ „ 0·1295 „

	Theory. $C_6H_{11}COOAg$.	Found. I.	Found. II.
Ag....	45·96 per cent.	45·84	45·98 per cent.

The *barium* salt was prepared by boiling the pure acid with an excess of baryta-water, passing carbonic anhydride, filtering, and evaporating the solution. It was thus obtained as a colourless syrup, which, even after standing for days over sulphuric acid, showed no signs of crystallising.

Action of Methyltetramethylene Dibromide on Ethylic Acetoacetate.

Ethylic Acetylmethylpentamethylenemonocarboxylate,

$$CH_2\begin{cases}CH_2—CH\cdot CH_3\\ CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5\end{cases}.$$

In studying this reaction, 50 grams of ethylic acetoacetate (2 mols.) and 46 grams of methyltetramethylene dibromide (1 mol.) were added to 10 grams of sodium (2 mols.) dissolved in 100 grams of absolute alcohol, and the whole heated in a flask connected with a reflux apparatus for 12 hours on a water-bath. The decomposition with ethylic acetoacetate takes place with much greater difficulty, and far less completely than when ethylic malonate is employed, so that even after long boiling the mixture still retained a decided alkaline reaction. At the end of 12 hours, the alcohol was distilled off, water

added and the oil extracted with ether as usual. The ethereal solution was washed with water, dried over calcic chloride, and the ether distilled off, when an almost colourless oil was obtained which on repeated fractioning was easily separated into two fractions, the lower of which, boiling below 200°, consisted of regenerated ethylic acetoacetate, whereas the higher one, boiling at 235—240°, was ethylic acetylmethylpentamethylenecarboxylate.

The substance prepared in this way is quite pure enough for further experiments, but owing to the presence of small quantities of bromine, it does not give good numbers on analysis. It was, therefore, for this purpose dissolved in a little alcohol, boiled with a small quantity of the sodium compound of ethylic acetoacetate for some hours, then reprecipitated and refractioned; as thus obtained, it is a colourless oil boiling constantly at 237—238°. Even after this treatment, it still contained traces of bromine, which made the analytical numbers somewhat unsatisfactory :—

0·1404 gram substance gave 0·3394 gram CO_2 and 0·1110 gram H_2O.

	Theory. $C_{11}H_{18}O_3$.	Found.
C	66·67 per cent.	65·93 per cent.
H	9·09 „	8·79 „
O	24·24 „	25·28 „

Ethyic acetylmethylpentamethylenecarboxylate is a thick colourless oil boiling at 237—238°, and possessing a strong, but not unpleasant odour. The yield of this substance obtained by the above reaction is very good indeed.

Hydrolysis of Ethylic Acetylmethylpentamethylenecarboxylate.

Formation of—

Methylpentamethylenecarboxylic Acid, $CH_2\langle \begin{matrix} CH_2—CH\cdot CH_3 \\ | \\ CH_2—CH\cdot COOH \end{matrix}$,

and of

Methylpentamethylene Methyl Ketone, $CH_2\langle \begin{matrix} CH_2—CH\cdot CH_3 \\ | \\ CH_2—CH\cdot CO\cdot CH_3 \end{matrix}$.

In carrying out this hydrolysis, the fraction of ethylic acetylmethylpentamethylenecarboxylate boiling at 235—240° was mixed with a large excess of a nearly concentrated solution of potash in pure alcohol, and boiled for two hours on a water-bath in a flask connected with a reversed condenser. On dissolving the product in water, acetylmethylpentamethylene methyl ketone was precipitated in oily drops,

and was easily separated from the solution of the potash salts by repeated extraction with ether.

The aqueous solution, which was first examined, was evaporated on a water-bath, until quite free from alcohol, acidified with dilute sulphuric acid, and the oily acid thus precipitated several times extracted with ether. The ethereal solution was well washed with water, dried over calcic chloride, and the ether distilled off, the resulting brownish-coloured oily acid being then purified by fractional distillation. It was thus easily obtained pure as a colourless oil boiling constantly at 220—221°, and possessing all the properties of the methylpentamethylenecarboxylic acid previously obtained from ethylic malonate and methyltetramethylene dibromide (see page 193). Analysis gave the following numbers :—

0·1856 gram substance gave 0·4442 gram CO_2 and 0·1540 gram H_2O.

	Theory. $C_6H_{11}(COOH)$.	Found.
C	65·62 per cent.	65·30 per cent.
H	9·38 „	9·21 „
O	25·00 „	25·49 „

Although this acid was evidently identical with that obtained from ethylic malonate, it was thought necessary to prove this fact more conclusively.

The sp. gr. and magnetic rotation of this specimen was therefore examined by W. H. Perkin (sen.) with the following results :—

$$d\frac{4°}{4°}\ 1·0256, \qquad d\frac{15°}{15°}\ 1·0172,$$

$$d\frac{10°}{10°}\ 1·0208, \qquad d\frac{20°}{20°}\ 1·0139.$$

$$d\frac{25°}{25°}\ 1·0109.$$

Magnetic Rotations.

	t.	Sp. rotation.	Mol. rotation.
	18°	0·9887	6·927
	18	0·9943	6·966
	18	0·9905	6·939
	18	0·9908	6·941
Average	18	0·9911	6·943

Although this specimen was small, and could therefore not be submitted to such repeated refractioning as was the case with the previous

sample, still on comparing the numbers obtained in the density determination and magnetic rotation of the two products, it will be seen that they agree sufficiently well to leave no doubt as to their identity.

The ethereal solution containing the methylpentamethylene methyl ketone, which had been separated from the potash salts as described above, was next examined. After well washing with water, drying over calcic chloride, and distilling off the ether, a brownish oil of aromatic odour was left behind; on distillation, it passed over almost entirely between 165° and 175°, and on repeated fractioning was easily obtained pure, as a colourless oil boiling constantly at 170—171°.

Analysis.

0·1547 gram substance gave 0·4326 gram CO_2 and 0·1550 gram H_2O.

	Theory. $C_6H_{11}CO{\cdot}CH_3$.	Found.
C	76·19 per cent.	76·27 per cent.
H	11·11 „	11·13 „
O	12·70 „	12·60 „

Methylpentamethylene methyl ketone is a colourless oil possessing in a very marked degree the penetrating odour of peppermint. It combines readily with phenylhydrazine and hydroxylamine, and dissolves, although with some difficulty, in bisulphite of soda.

The sp. gr. and magnetic rotations of this interesting compound were also examined by W. H. Perkin (sen.), who gave us the following as the result of his experiments:—

$$d\frac{4^\circ}{4^\circ}\ 0{\cdot}9222, \qquad d\frac{15^\circ}{15^\circ}\ 0{\cdot}9136,$$

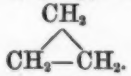
$$d\frac{10^\circ}{10^\circ}\ 0{\cdot}9174, \qquad d\frac{20^\circ}{20^\circ}\ 0{\cdot}9100,$$

$$d\frac{25^\circ}{25^\circ}\ 0{\cdot}9070.$$

Magnetic Rotations.

	t.	Sp. rotation.	Mol. rotation.
	18°	1·0450	8·026
	18	1·0452	8·025
	18	1·0432	8·012
	18	1·0431	8·012
Average	18	1·0441	8·019

Action of Sodium on Methyltetramethylene Dibromide.

In his researches on the action of sodium on trimethylene bromide, Freund (*Monats.*, 1882, 622) obtained a gas which differed in its properties in a very marked way from ordinary propylene, and which he therefore considered to be trimethylene, 

Following up this reaction, we have submitted methyltetramethylene dibromide to the action of sodium, and obtained a hydrocarbon boiling at 39—42°, which from its mode of formation is most probably methyltetramethylene—

$$\begin{matrix}CH_2\cdot CH(CH_3)Br\\ |\\ CH_2\cdot CH_2Br\end{matrix} + Na_2 = \begin{matrix}CH_2—CH\cdot CH_3\\ |\quad\quad |\\ CH_2—CH_2\end{matrix} + 2NaBr.$$

At the same time, owing to the small quantity of material at our disposal, we have not been able to prove that this really is the constitution of the substance, and we therefore use the name methyltetramethylene only provisionally, until we have been able more fully to study its properties.

If methyltetramethylene dibromide is warmed with finely divided sodium, a most violent reaction takes place, but in order to isolate the product, this must be very much moderated. After several experiments, the following method was found to give good results:—

10 grams of clean sodium were heated under toluene in a loosely stoppered flask until completely melted, the stopper then lightly inserted, and the whole vigorously shaken until the sodium had assumed the appearance of fine metallic sand.

The contents of the flask were then transferred to a Würtz flask (holding about 120—150 c.c.), fitted with a dropping funnel and supplied with a condenser, through which ice-water was run during the whole of the subsequent operation.

The toluene (20 grams) in which the sodium was suspended, was then heated nearly to boiling, the flame taken away, and a mixture of 30 grams of methyltetramethylene dibromide and 20 grams of toluene dropped in slowly through the dropping funnel. The reaction is sufficiently violent to keep the liquid boiling briskly. During the decomposition, a small quantity of liquid of low-boiling point condenses, and is collected in a small flask cooled in a freezing mixture. As soon as all the bromide has been added, the product is gently distilled, until about $\frac{1}{3}$ of the toluene has passed over. In order to separate the methyltetramethylene from this excess of toluene, the crude distillate was subjected to repeated fractioning

from a Würtz flask provided with a very long neck, and in this way an oil was at last obtained which boiled constantly at 39—42°.

The combustion, which was carried out in a very long combustion tube, gave the following numbers :—

0·1864 gram substance gave 0·2454 gram H_2O and 0·5830 gram CO_2.

	Theory. C_5H_{10}.	Found.
C.....	85·71 per cent.	85·30 per cent
H.....	14·29 „	14·62 „

Methyltetramethylene is a very volatile substance boiling at 39—42°, and has an odour very similar to that of the hydrocarbons of the methane series. When mixed with very concentrated aqueous hydrogen iodide, the volume of the hydrocarbon decreased slightly during the first day, but afterwards did not appear to be acted on any further. This fact seems to show that this hydrocarbon, although it may contain a small quantity of an unsaturated compound, is itself saturated. It is isomeric with normal amylene,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$$

(boiling point 39—40°), but not identical, as the latter is easily and completely absorbed by concentrated aqueous hydrogen iodide with formation of the iodide of methyl propyl carbinyl.

A possible explanation of the formation of the hydrocarbon above described, by the action of sodium on methyltetramethylene dibromide was, that in the presence of small quantities of water nascent hydrogen might be formed, which would react on the dibromide, forming pentane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

In order to avoid a reduction such as this, great care was taken to have all the materials as well as the apparatus perfectly dry, and the result of the analysis of the product obtained shows conclusively that it cannot be pentane, which requires C = 83·33 per cent., H = 16·66 per cent.

XX.—*The Synthetical Formation of Closed Carbon-chains.* Part IV. *Some Derivatives of Hexamethylene.*

By Paul C. Freer, Ph.D., and W. H. Perkin (Jun.), Ph.D.

In a previous paper by one of us (Trans., **51**, 704), it was shown that methyldehydrohexonecarboxylic acid when boiled with water yields acetobutyl alcohol, thus :—

$$\begin{array}{l} CH_3\cdot C(=CH_2)\cdot O\cdot CH_2 \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} + H_2O =$$
$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH + CO_2.$$

This acetobutyl alcohol, when treated with sodium amalgam, is easily converted into δ-hexylene glycol, thus :—

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH + H_2 =$$
$$CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH.$$

If this glycol is digested with concentrated aqueous hydrogen bromide, methylpentamethylene dibromide is obtained, according to the following equation :—

$$CH_3\cdot CH(OH)\cdot[CH_2]_3\cdot CH_2OH + 2HBr =$$
$$CH_3\cdot CHBr\cdot[CH_2]_3\cdot CH_2Br + 2H_2O.$$

By the action of the sodium compound of ethylic malonate on this dibromide, hexamethylene-derivatives can be obtained, the reaction being exactly similar to that described in the previous paper for the formation of pentamethylene-derivatives from methyltetramethylene dibromide, thus :—

$$2CHNa(COOC_2H_5)_2 + CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br =$$
$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot C(COOC_2H_5)_2 \end{array} + CH_2(COOC_2H_5)_2 + 2NaBr,$$

Ethylic methylhexamethylene-dicarboxylate (2, 1, 1).

ethylic methylhexamethylenedicarboxylate being formed.

This ethereal salt on hydrolysis yields the free methylhexamethylenedicarboxylic acid which, when distilled, is decomposed into methylhexamethylenemonocarboxylic acid and carbonic anhydride, thus :—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot C(COOH)_2 \end{array} = \begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot CH\cdot COOH \end{array} + CO_2.$$

Methylhexamethylenemono-carboxylic acid.

In carrying out this investigation, it was again thought that interesting results might be obtained from the study of the action of methylpentamethylene dibromide on the sodium compound of ethylic acetoacetate, in order to determine whether hexamethylene-derivatives would result, or whether oxygen-rings would be formed, as in the case of trimethylene dibromide.

If one molecular proportion of the sodium compound of ethylic acetoacetate be digested with one molecular proportion of methylpentamethylene dibromide, a substance, $C_{12}H_{21}BrO_3$, will be produced which may have either of the two following constitutional formulæ:—

(1.) $\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!\!>\!CH\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br.$

(2.) $\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!\!>\!CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_3.$

No attempts were made to distinguish between these two formulæ, as this question has no bearing on the constitution of the substances subsequently obtained from this intermediate compound.

If this bromo-compound is treated with zinc-dust and acetic acid, the bromine-atom is easily displaced by hydrogen. In order to determine its constitution, therefore, it would only be necessary to isolate this reduction product and ascertain whether it is isomeric or identical with ethylic hexylacetoacetate; in the former case formula (1), in the latter formula (2) would be correct.

This compound, $C_{12}H_{21}BrO_3$, when treated with sodic ethylate or the sodium-compound of ethylic acetoacetate, is converted into ethylic acetylmethylhexamethylene carboxylate, thus:—

$$\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!\!>\!CH\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br + C_2H_5\cdot ONa$$

$$= \begin{matrix}CH_3—CH_2—CH\cdot CH_3\\ |\qquad\qquad\quad |\\ CH_2—CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5\end{matrix} + NaBr + C_2H_5\cdot OH.$$

Ethylic acetylmethylhexamethylene-carboxylate (1, 2, 1).

In preparing this compound, however, it is much easier to start with 2 mols. of ethylic acetoacetate and 1 mol. of methylpentamethylene dibromide, in which case the reaction would be represented thus:—

$$2\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!\!>\!CHNa + CH_3\cdot CH(Br)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$$

$$= \begin{matrix}CH_2—CH_2—CH\cdot CH_3\\ |\qquad\qquad\quad |\\ CH_2—CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5\end{matrix} + CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + 2NaBr.$$

That the product of this reaction really is a hexamethylene-derivative is shown by a study of the products resulting from its hydrolysis. When boiled with alcoholic potash, ethylic acetylmethylhexamethylene-carboxylate is easily decomposed with formation of methylhexa-

methylene methyl ketone and methylhexamethylenecarboxylic acid, thus:—

(1.) $$\begin{matrix}CH_2—CH_2—CH\cdot CH_3\\ |\qquad\quad |\\ CH_2—CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5\end{matrix} + 2KOH =$$

$$\begin{matrix}CH_2—CH_2—CH\cdot CH_3\\ |\qquad\quad |\\ CH_2—CH_2—CH\cdot CO\cdot CH_3\end{matrix} + C_2H_5\cdot OH + K_2CO_3.$$

Methylhexamethylene methyl ketone (2, 1).

(2.) $$\begin{matrix}CH_2—CH_2—CH\cdot CH_3\\ |\qquad\quad |\\ CH_2—CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5\end{matrix} + 2KOH =$$

$$\begin{matrix}CH_2—CH_2—CH\cdot CH_3\\ |\qquad\quad |\\ CH_2—CH_2—CH\cdot COOK\end{matrix} + CH_3\cdot COOK + C_2H_5\cdot OH.$$

Potassic methylhexamethylene-carboxylate (2, 1).

The methylhexamethylenecarboxylic acid obtained in this way showed all the reactions and possessed the same properties as that obtained from ethylic malonate and methylpentamethylene dibromide.

Unfortunately, owing to the small quantity of material at our disposal no physical measurements could be made with the sample obtained from ethylic acetoacetate, which would have afforded some more definite proof as to the identity of the two acids. But from a study of the results obtained by Colman and Perkin (see previous paper) in their experiments on the action of methyltetramethylene dibromide on ethylic malonate and acetoacetate, there can scarcely be a doubt that in the present case also, hexamethylene-derivatives are formed in both the reactions described above.

Methylpentamethylene Dibromide, $CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$.

The formation of methylpentamethylene dibromide (δ-hexylene dibromide) from δ-hexylene glycol has been briefly noticed in a previous paper (Trans., **51**, 722).

In preparing considerable quantities of this dibromide, the following method was found to give the best results:—

δ-Hexylene glycol, prepared by the reduction of acetobutyl alcohol as previously described (Trans., **51**, 722), is dissolved in five times its volume of concentrated aqueous hydrogen bromide (sp. gr. 1·85) and gently heated to boiling in a flask connected with a reflux apparatus, a slow stream of hydrogen bromide being passed into the liquid during the operation. After heating for about an hour, the whole is

allowed to cool, diluted with water, and the precipitated dark-brown-coloured bromide extracted several times with ether. The ethereal solution is then dried over calcic chloride, the ether distilled off, and the crude bromide purified by fractional distillation under reduced pressure (100 mm.), when it is easily obtained pure, boiling constantly at 153—154° (100 mm.).

In preparing this dibromide for the following experiments, a method exactly similar to that described under "Methyltetramethylene Dibromide" (in the paper by Colman and Perkin), was first used, but afterwards it was found that as δ-hexylene glycol could be so much more completely extracted from its aqueous solution by ether than γ-pentylene glycol can, the tedious method there described was not necessary.

Ethylic Methylhexamethylenedicarboxylate

$$\begin{array}{l} CH_2—CH_2—CH\cdot CH_3 \\ \quad\quad\quad\

of disagreeable odour, boiling at 260—265°. The yield is not very good, owing to the formation of a considerable quantity of a high boiling substance. In a later experiment, where 45 grams of ethylic malonate, 34 grams of methylpentamethylene dibromide, and 6·4 grams of sodium were used, 56 grams of crude product was obtained on extraction with ether. This, on fractioning under 160 mm. pressure, gave 39 grams of oil boiling below 250°; on refractioning under ordinary pressures, 20 grams of crude ethylic methylhexamethylene dicarboxylate were obtained, boiling at 245—275°. In both the experiments, it was found that the oil obtained boiling at 260—265°, and which was supposed to be pure, still contained traces of bromine which seriously affected the analytical results. The product analysed was first freed from bromine by long boiling with a little ethylic malonate and sodic ethylate, and subsequent treatment with zinc-dust and acetic acid.

Methylhexamethylenedicarboxylic Acid, $\begin{matrix} CH_2—CH_2—CH\cdot CH_3 \\ | \qquad\qquad\quad | \\ CH_2—CH_2—C(COOH)_2 \end{matrix}$.

In order to obtain the free dicarboxylic acid, the fraction of the ethereal salt boiling at 258—267° was mixed with an excess of alcoholic potash, containing twice the calculated quantity of pure potash dissolved in pure alcohol, and boiled on a water-bath for six hours. The excess of alcohol was then distilled off, the residue dissolved in water and evaporated till quite free from alcohol. The slightly brownish-coloured liquid was nearly neutralised with dilute sulphuric acid, filtered, the filtrate mixed with an excess of dilute sulphuric acid and several times extracted with ether. The ethereal solution, after drying and evaporating, deposited the crude acid as a thick yellowish oil, which, on standing for some days over sulphuric acid in a vacuum, almost entirely solidified. This crude product was first roughly separated from oily impurities by spreading out on a porous plate, and the resulting almost colourless crystalline mass once or twice recrystallised from water. It was thus obtained as a sandy crystalline powder, which on analysis gave the following numbers:—

I. 0·1995 gram substance gave 0·4246 gram CO_2 and 0·1377 gram H_2O.

II. 0·1772 gram substance gave 0·3770 gram CO_2 and 0·1217 gram H_2O.

	Theory. $C_7H_{12}(COOH)_2$.	Found. I.	Found. II.
C	58·06 per cent.	58·04	58·02
H	7·53 „	7·67	7·63
O	34·41 „	34·29	34·35

Methylhexamethylenedicarboxylic acid melts at about 147°, being at the same time partially decomposed into methylhexamethylenemonocarboxylic acid and carbonic anhydride. Methylhexamethylenedicarboxylic acid is readily soluble in ether, alcohol, and hot water, but more sparingly in cold water.

This acid has, especially when not quite pure, a great tendency to form supersaturated solutions—a fact which renders its purification a matter of considerable difficulty. From its solution in water, it is slowly deposited in crystalline crusts, which consist of a mass of small hard crystals. Methylhexamethylenedicarboxylic acid shows little tendency to form large crystals, and in this respect differs in a very marked manner from the corresponding pentamethylene-derivative.

The silver salt of this acid was prepared in the usual way, by precipitating a neutral solution of the ammonium salt with nitrate of silver, collecting the white amorphous precipitate thus obtained, washing it well with water, and drying over sulphuric acid in a vacuum.

The following result was obtained on analysis:—

0·3102 gram substance gave 0·1662 gram Ag.

Theory. $C_7H_{12}(COOAg)_2$.	Found.
54·00 per cent.	53·54 per cent.

Methylhexamethylenemonocarboxylic Acid,

$$\begin{array}{l} CH_2—CH_2—CH\cdot CH_3 \\ \quad\quad\quad\quad\quad\quad\quad\quad | \\ CH_2—CH_2—CH\cdot COOH. \end{array}$$

In preparing this acid, the pure dicarboxylic acid is melted in a small Würtz flask, and then gently heated in a metal-bath until the decomposition into carbonic anhydride and methylhexamethylenemonocarboxylic acid is complete. The residual oil on fractioning all distils over between 230° and 240°, and on repeated fractioning the new acid is obtained pure, as a colourless oil boiling constantly at 235—236°.

Analyses:—

I. 0·1987 gram substance gave 0·4894 gram CO_2 and 0·1752 gram H_2O.

II. 0·2156 gram substance gave 0·5320 gram CO_2 and 0·1892 gram H_2O.

III. 0·1814 gram substance gave 0·4483 gram CO_2 and 0·1599 gram H_2O.

	Theory. $C_7H_{13}(COOH)$.	Found. I.	II.	III.
C	67·61 per cent.	67·17	67·25	67·34
H.....	9·86 „	9·79	9·75	9·79
O.....	22·53 „	23·04	23·00	22·87

Methylhexamethylenemonocarboxylic acid is a thick colourless oil of most penetrating and disagreeable odour, which is even more pronounced than that of the pentamethylene-derivative. It boils at 235—236°.

Its sp. gr. and magnetic rotation have been determined by W. H. Perkin (sen.), who gave us the following account of his experiments:—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}0079, \qquad d\frac{15^\circ}{15^\circ}\ 0{\cdot}99982,$$

$$d\frac{10^\circ}{10^\circ}\ 1{\cdot}0033, \qquad d\frac{20^\circ}{20^\circ}\ 0{\cdot}9966,$$

$$d\frac{25^\circ}{25^\circ}\ 0{\cdot}9940.$$

Magnetic Rotations.

	t.	Sp. rotation.	Mol. rotation.
	18·0°	1·0073	7·965
	18·0	1·0106	7·991
	18·0	1·0103	7·989
	18·5	1·0100	7·990
	18·5	1·0052	7·952
	17·0	1·0079	7·962
Average	18·0	1·0085	7·975

With regard to the constitution of this acid, the same might be said as was said of the constitution of methylpentamethylenecarboxylic acid (pp. 195—196).

From its mode of formation, this acid might be an unsaturated compound, in which case its constitution would be represented by one of the two following formulæ:—

(1.) $COOH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2$.
(2.) $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2$.

The acid represented by formula (2) is allylacetic acid, plus $3CH_2$ or $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2 + 3CH_2$.

Its magnetic rotation would therefore be calculated thus:—

Magnetic rotation of allylacetic acid	6·426
$+ 3CH_2 = 3 \times 1·023$	3·069
Calc. rotation.....	9·495

An acid of the constitution represented in formula (2) would therefore have a calculated rotation of 9·495, whereas an acid with the constitution represented in formula (1) would have a rotation still larger, probably 9·615.

The difference between these two numbers and that actually found (*i.e.*, 7·975) is so great as to entirely preclude the possibility of the acid described above as methylhexamethylenecarboxylic acid being an unsaturated compound.

That methylhexamethylenecarboxylic acid and methylpentamethylenecarboxylic acid are analogously constituted, can also be easily deduced from the numbers found as the magnetic rotation of each, thus:—

Magnetic rotation of methylhexamethylenecarboxylic acid	7·975
Magnetic rotation of methylpentamethylenecarboxylic acid	6·914
Difference for CH_2	1·061

Now the actual value of CH_2 as a difference between two analogously constituted substances is 1·023, a number very closely agreeing with that found above.

Methylhexamethylenecarboxylic acid is a more feeble acid even than the corresponding pentamethylene-derivative. If the solution of its ammonium salt is evaporated over sulphuric acid in a vacuum, it is almost entirely decomposed into the free acid and ammonia.

In order, therefore, to prepare the silver salt, the free acid was dissolved in an excess of ammonia, neutralised with dilute nitric acid, and a small quantity of the silver salt first precipitated by the addition of a few drops of nitrate of silver. This was filtered off, and the bulk of the salt precipitated by adding an excess of silver nitrate to the filtrate. The bulky, white precipitate thus obtained, after well washing, and drying over sulphuric acid in a vacuum, gave the following results on analysis:—

0·2070 gram substance gave 0·0980 gram H_2O, 0·2950 gram CO_2, and 0·0898 gram Ag.

	Theory. $C_7H_{13}(COOAg)$.	Found.
C	38·55 per cent.	38·86 per cent.
H	5·22 „	5·26 „
Ag	43·37 „	43·37 „
O	12·85 „	12·51 „

Ethylic Bromomethylpentamethyleneacetoacetate,

$$\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!\!>\!CH\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br\ (?).$$

This substance, which is the primary product of the action of methylpentamethylene dibromide on ethylic acetoacetate, is prepared in the following way:—

2·3 grams of sodium are dissolved in 30 grams of absolute alcohol, and when quite cool mixed with 13 grams of ethylic acetoacetate and 24·5 grams of methylpentamethylene dibromide, and the whole heated on a water-bath for about two hours, at the end of which time the decomposition is usually completed. After distilling off the excess of alcohol, water is added, and the heavy oil thus precipitated is extracted two or three times with pure ether. The ethereal solution is well washed, carefully dried over calcic chloride, and the ether distilled off; in this way a colourless oil is obtained, which consists of nearly pure ethylic bromomethylpentamethyleneacetoacetate.

For the following analysis, a sample was taken which had been allowed to stand over sulphuric acid in a vacuum for some days, so as to free it completely from alcohol and ether:—

0·1944 gram substance gave 0·1242 gram AgBr.

	Theory. $C_{12}H_{21}BrO_3$.	Found.
Br.....	27·31 per cent.	27·15 per cent.

Ethylic bromomethylpentamethyleneacetoacetate, when freshly prepared, is a thick, colourless oil of disagreeable odour, which on keeping, especially when exposed to the air, soon assumes a brownish colour. When boiled with sodic ethylate, it is completely converted into a new compound free from bromine; this boils at 255—260°, and appears to be identical with ethylic acetylmethylhexamethylenecarboxylate.

If the bromo-compound is heated in a paraffin-bath at 250—270°, in a flask connected with a condenser, hydrogen bromide comes off regularly for some hours. In order to examine the product of this reaction, the heating was continued until the evolution of hydrogen bromide ceased, and the residue was examined. During the experiment, the oil, which was colourless to start with, had become dark brown, but on fractioning nearly the whole of it passed over between 255° and 260°, as a colourless oil, which now contained traces only of bromine. It is a matter of interest to ascertain whether this substance is identical or isomeric with ethylic acetylmethylhexamethylenecarboxylate, and experiments instituted with the object of deciding this question are in progress.

Ethylic Acetylmethylhexamethylenecarboxylate,

$$\begin{array}{l} CH_2—CH_2—CH\cdot CH_3 \\ \quad\quad\quad\quad\quad\quad\quad\quad | \\ CH_2—CH_2—C(CO\cdot CH_3)\cdot COOC_2H_5. \end{array}$$

In studying the action of methylpentamethylene dibromide on the sodium-compound of ethylic acetoacetate, the following quantities were used:—

Ethylic acetoacetate	26·0 grams.
Sodium	4·6 „
Methylpentamethylene dibromide	24·4 „

The sodium was dissolved in 50 grams of absolute alcohol, and to the resulting solution of sodic ethylate, when cold, the ethylic acetoacetate and the methylpentamethylene dibromide were added. The whole was then heated on a water-bath, in a flask connected with a reflux apparatus for 20 hours. At the end of this time, the excess of alcohol was distilled off, the residue treated with water, and two or three times extracted with ether. The ethereal solution, after drying over calcic chloride and evaporating, deposited an almost colourless oil, which, when submitted to repeated fractional distillation, was easily separated into two portions, an oil boiling at 180—200°, and consisting of regenerated ethylic acetoacetate, and a second fraction of the boiling point 255—260°, which consisted of ethylic acetylmethylhexamethylenecarboxylate.

The product, even after repeated refractionation, was found to contain small quantities of bromine, amounting sometimes to as much as 2—3 per cent. In order to get satisfactory analytical numbers, it was found necessary to submit this fraction, 255—260°, to prolonged boiling with small quantities of the sodium compound of ethylic acetoacetate, and then, to remove the last traces, to reduction with a little zinc and acetic acid. The sample used in the following analysis boiled at 255—257°.

0·1688 gram substance gave 0·4171 gram CO_2 and 0·1428 H_2O.

	Theory. $C_{12}H_{20}O_3$.	Found.
C	67·92 per cent.	67·38 per cent.
H	9·43 „	9·40 „
O	22·64 „	23·22 „

Ethylic acetyl methylhexamethylenecarboxylate is a thick colourless oil of a peculiar but not disagreeable odour, strongly resembling that of the corresponding pentamethylene-derivative. The yield

obtained is very good, but it was found impossible to get it quite free from bromine without reducing with zinc and acetic acid, except by boiling with large quantities of sodic ethylate and ethylic acetoacetate, in which case great loss is sustained owing to hydrolysis setting in.

The crude product of the reaction, however, rarely contains more than 1 or 2 per cent. of bromine and is quite pure enough for subsequent experiments.

Hydrolysis of Ethylic Acetylmethylhexamethylenecarboxylate.

Methylhexamethylenecarboxylic Acid, $\begin{matrix} CH_2—CH_2—CH\cdot CH_3 \\ | \qquad\qquad | \\ CH_2—CH_2—CH\cdot COOH. \end{matrix}$

Methylhexamethylene Methyl Ketone, $\begin{matrix} CH_2—CH_2—CH\cdot CH_3 \\ | \qquad\qquad | \\ CH_2—CH_2—CH\cdot CO\cdot CH_3. \end{matrix}$

Just as ethylic acetylmethylpentamethylenecarboxylate when subjected to hydrolysis is split up and yields methylpentamethylenecarboxylic acid and methylpentamethylene methyl ketone (see previous paper, p. 198), so the corresponding hexamethylene-derivative when treated with alcoholic potash is converted into methylhexamethylenecarboxylic acid and methylhexamethylene methyl ketone.

In studying this decomposition, the fraction of ethylic acetylmethylhexamethylenecarboxylate boiling at 255—260° was mixed with a considerable excess of very concentrated alcoholic potash, and heated on a water-bath for about four hours in a flask connected with a reflux apparatus. In a short time, the mass became quite thick owing to the separation of carbonate, so that it was found advisable from time to time to disconnect the condenser, cork up the flask, and shake well. As soon as the decomposition was complete, the product was allowed to cool, mixed with about three times its volume of water, and several times extracted with ether.

The aqueous solution, which was first examined, was evaporated on a water-bath till quite free from ether and alcohol, acidified with dilute sulphuric acid, and repeatedly extracted with pure ether. The ethereal solution after drying over calcic chloride and evaporating deposited a small quantity of a brownish-coloured oil which on distillation boiled almost entirely between 230° and 240°. On refractioning, the greater part was obtained as a thick oil boiling at 234—237°. This on analysis gave the following numbers, which agree with those required for methylhexamethylenecarboxylic acid:—

0·1763 gram substance gave 0·4340 gram CO_2 and 0·1576 gram H_2O.

	Theory. $C_8H_{14}O_2$.	Found.
C	67·60 per cent.	67·14 per cent.
H	9·86 „	9·93 „
O	22·53 „	22·93 „

The acid obtained by this reaction possesses all the properties of the methylhexamethylenecarboxylic acid obtained from ethyl malonate and methylpentamethylene dibromide. It has the same disagreeable and penetrating odour and the same boiling point (234—237°). It is unfortunate that the amount obtained was not sufficient to allow of its magnetic rotation being determined, in order thus to be able to make sure of the identity of the two samples.

The ethereal extract which had been separated from the aqueous solution of the potash salts, as described above, was next examined. After washing with water, drying over calcic chloride and evaporating, a considerable quantity of a yellowish oil was obtained, which on fractioning boiled almost constantly at 197—200°, and gave the following numbers on analysis :—

I. 0·1576 gram substance gave 0·1630 gram H_2O and 0·4432 gram CO_2.

II. 0·1497 gram substance gave 0·1580 gram H_2O and 0·4206 gram CO_2.

	Theory. $C_9H_{16}O$.	Found. I.	Found. II.
C	77·14 per cent.	76·71	76·56
H	11·43 „	11·49	11·72
O	11·43 „	11·80	11·72

Methylhexamethylene methyl ketone is a colourless oil, possessing in a concentrated state a most penetrating odour, somewhat resembling that of peppermint, but when present only in small quantities its odour reminds one of that of new-mown hay.

It combines with phenylhydrazine and apparently also with sodic bisulphite, but neither of the compounds produced have as yet been examined.

Action of Sodium on Methylpentamethylene Dibromide.

In studying this decomposition, the experiment was carried out in a way exactly similar to that described in the last paper (p. 201) in the case of methyltetramethylene dibromide.

After submitting the product to the most careful fractional distilla-

tion, an oil was at last obtained boiling constantly at 70—71°; this gave the following results on analysis:—

0·2045 gram substance gave 0·2688 gram H_2O and 0·6389 gram CO_2.

	Theory. C_6H_{12}.	Found.
C.....	85·71 per cent.	85·21 per cent.
H	14·29 „	14·61 „

These numbers therefore agree with those required for methylpentamethylene, which should have been formed had the reaction taken place according to the following equation:—

$$\begin{matrix} CH_3—CH_2Br \\ | \\ CH_2—CH_2\cdot CHBr\cdot CH_3 \end{matrix} + Na_2 = \begin{matrix} CH_2—CH_2 \\ | \quad\quad \diagdown \\ CH_2—CH_2 \end{matrix} \!\!> CH\cdot CH_3 + 2NaBr.$$

At present, however, no definite proof can be given that the hydrocarbon has this constitution. It is isomeric with the hexylenes, C_6H_{12}, several of which are known, and which boil from 67° to 73°, but it differs from them in this respect, that even after standing for some weeks with concentrated aqueous hydrogen iodide it is not acted on. By a further study of this interesting substance it is hoped that the question as to its constitution will be definitely settled.

XXI.—*The Synthetical Formation of Closed Carbon-chains.* Part V. *Experiments on the Synthesis of Heptamethylene-derivatives.*

By Paul C. Freer, Ph.D., and W. H. Perkin, jun., Ph.D.

When ethylic malonate is treated with methyltetramethylene dibromide, the only product of the reaction is ethylic methylpentamethylenedicarboxylate, but when methylpentamethylene dibromide is used, besides ethylic methylhexamethylenedicarboxylate, a considerable quantity of a second substance is formed, which is the product of the action of 1 mol. of methylpentamethylene dibromide on 2 mols. of ethylic malonate, thus:—

$$2(COOC_2H_5)_2CHNa + CH_3\cdot CHBr\cdot[CH_2]_3\cdot CH_2Br = (COOC_2H_5)_2CH\cdot CH(CH_3)\cdot[CH_2]_4\cdot CH(COOC_2H_5)_2 + 2NaBr.$$

This ethereal salt, for which we propose the name ethylic isoheptane-$\omega_2\omega_2$-tetracarboxylate, is converted by hydrolysis into the corre-

sponding acid, and this on heating to 200° is split up into carbonic anhydride and a new acid of the succinic series (methylazelaic acid)—

$$(COOH)_2CH\cdot CH(CH_3)\cdot[CH_2]_4\cdot CH(COOH)_2 =$$

Isoheptanetetracarboxylic acid.

$$COOH\cdot CH_2\cdot CH(CH_3)\cdot[CH_2]_5\cdot COOH + 2CO_2.$$

Methylazelaic acid.

Ethylic isoheptanetetracarboxylate was for these researches of special importance, because, as will be seen from a glance at its formula, it contains two hydrogen-atoms which, from their position with regard to the carb-ethoxyl-groups, are capable of being displaced by sodium, forming a disodium compound of the following formula :—

$$(COOC_2H_5)_2CNa\cdot CH(CH_3)\cdot[CH_2]_4CNa(COOC_2H_5)_2.$$

This disodium compound when treated with iodine or bromine should be converted into ethylic methylheptamethylenetetracarboxylate,* thus :—

$$(COOC_2H_5)_2CNa\cdot CH(CH_3)\cdot[CH_2]_4\cdot CNa(COOC_2H_5)_2 + Br_2 =$$

$$CH_2\begin{<}\begin{matrix}CH_2\cdot CH(CH_3)—C(COOC_2H_5)_2\\ |\\ CH_2—CH_2—C(COOC_2H_5)_2\end{matrix}\end{<} + 2NaBr.$$

Methylheptamethylenetetracarboxylate (1, 1, 2, 2).

This ethylic salt on hydrolysis would then yield the corresponding tetracarboxylic acid, which on heating to 200° would be converted into methylheptamethylenedicarboxylic acid (1, 2) and carbonic anhydride, thus :—

$$CH_2\begin{<}\begin{matrix}CH_2\cdot CH(CH_3)—C(COOH)_2\\ |\\ CH_2—CH_2—C(COOH)_2\end{matrix}\end{<} =$$

Methylheptamethylenetetracarboxylic acid (3, 1, 1, 2, 2).

$$CH_2\begin{<}\begin{matrix}CH_2\cdot CH(CH_3)—CH\cdot COOH\\ |\\ CH_2—CH_2—CH\cdot COOH\end{matrix}\end{<} + 2CO_2.$$

Methylheptamethylenedicarboxylic acid (3, 1, 2).

To prove that such a change had taken place, it would be only necessary to show (1) that the resulting methylheptamethylenedicarboxylic acid differed in its properties from the methylazelaic acid produced by the hydrolysis of ethylic isoheptanetetracarboxylate

* Compare the formation of ethylic tetramethylenetetracarboxylate from ethylic butane-$\omega_2\omega_2$-tetracarboxylate (Trans., 51, 18), also of ethylic pentamethylene-tetracarboxylate from ethylic pentane-$\omega_2\omega_2$-tetracarboxylate (Trans., 51, 240).

before its treatment with sodium and bromine; and (2) that the resulting acid was capable of forming an anhydride, thus proving that the two carboxyl-groups which at first were separated by seven carbon-atoms, were now in the ortho-position.

Two careful experiments were tried with the object of carrying out this synthesis (bromine being used), but, although, from the decolorisation of every drop of bromine as it came in contact with the sodium compound, it seemed as though the decomposition had taken place in the way desired, on examining the product it was found that no heptamethylene-ring had been formed.

The resulting ethereal salt was a mixture containing a considerable quantity of regenerated ethylic isoheptanetetracarboxylate and some very high-boiling complex products. It is impossible at the present stage of these experiments to explain what really takes place in a reaction of this kind;* the only clear point is, that as far as we could tell, no trace of a heptamethylene-derivative is produced. This research does not of course prove that a closed carbon-chain of seven atoms cannot be formed; but it would nevertheless appear to throw doubt on the existence of a chain of these dimensions. Experiments are being carried on, the results of which it is hoped will clearly settle this important point.

Ethylic Isoheptanetetracarboxylate,

$(COOC_2H_5)_2CH{\cdot}CH(CH_3){\cdot}[CH_2]_4{\cdot}CH(COOC_2H_5)_2$.

When the product of the action of methylpentamethylene dibromide on ethylic malonate is distilled, as described in the previous paper (p. 206), ethylic methylhexamethylenedicarboxylate passes over, whilst a thick, yellowish oil remains behind, consisting of crude ethylic isoheptanetetracarboxylate. If this crude residue be submitted to fractional distillation under a pressure of 60 mm., nearly the whole of it will pass over without the slightest decomposition between 265° and 285°, and on once or twice refractioning the oil is easily obtained pure boiling at 273—276°.

Analysis.

0·1808 gram substance gave 0·3970 gram CO_2 and 0·1408 gram H_2O.

	Theory. $C_{20}H_{34}O_8$.	Found.
C	59·70 per cent.	59·83 per cent.
H	8·45 „	8·65 „
O	31·84 „	31·52 „

* Compare for similar experiments, Kipping (this vol., pp. 22 and 23).

Ethylic isoheptanetetracarboxylate is a thick, colourless syrup boiling at 273—276° (60 mm.).

When dissolved in ether and treated with 2 mols. of sodic ethylate, a yellowish-white sodium compound is precipitated. Several attempts were made to analyse this, but it was found to be impracticable, owing to its being so soluble in ether and so hygroscopic.

Methylazelaic Acid, $COOH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}[CH_2]_5{\cdot}COOH$.

When treated with alcoholic potash, ethylic isoheptanetetracarboxylate is readily hydrolysed. In carrying out this hydrolysis, 20 grams of the pure ethereal salt was mixed with a solution of 20 grams of pure potash dissolved in pure methyl alcohol, and boiled in a flask connected with a reflux apparatus for about six hours. The excess of alcohol was then distilled off, the residue dissolved in water, the resulting colourless solution neutralised with dilute sulphuric acid and evaporated on a water-bath till quite free from alcohol and ether. Excess of sulphuric acid was then added, and the isoheptanetetracarboxylic acid extracted at least 20 times with pure ether. The ethereal solution after drying over calcic chloride and evaporating, deposited the free acid as a thick, colourless syrup, which was not analysed, but at once converted into methylazelaic acid.

In order to do this, the flask containing the isoheptanetetracarboxylic acid was heated in a metal bath slowly to 200°, and kept at that temperature until the evolution of carbonic anhydride had entirely ceased. The resulting brownish-coloured oil was dissolved in a little water, boiled with a small quantity of animal charcoal, and the almost colourless solution evaporated on a water-bath. As, however, the residue, even after standing for some days over sulphuric acid in a vacuum, showed no signs of crystallisation, it was further purified by conversion into the ethereal salt. For this purpose, the crude substance was dissolved in pure ethyl alcohol, saturated with hydrogen chloride, and allowed to stand for some hours. Water was then added, the ethereal salt extracted with ether, washed with dilute carbonate of soda solution, the ether distilled off, and the residue fractioned under reduced pressure (100 mm.). In this way it was easily obtained pure as a thick oil boiling at 212—215° (100 mm.).

Analysis.

0·1655 gram substance gave 0·1500 gram H_2O and 0·3936 gram CO_2.

	Theory. $C_{14}H_{26}O_4$.	Found.
C.....	65·11 per cent.	64·89 per cent.
H.....	10·08 „	10·07 „
O.....	24·81 „	25·04 „

The ethylic salt of methylazelaic acid is a colourless liquid of peculiar odour, and boils at 212—215° under a pressure of 100 mm. It is isomeric with ethylic sebate, which boils at 307—308° under ordinary pressures.

In order to obtain methylazelaic acid, the ethereal salt was gently boiled with a slight excess of a solution of potash in pure methyl alcohol for two hours, the excess of alcohol distilled off, the product dissolved in water and the solution evaporated nearly to dryness. The residue was then dissolved in a little water, acidified with dilute sulphuric acid, and extracted two or three times with pure ether. The ethereal solution after being carefully dried over calcic chloride was evaporated, and in this way the new acid was obtained as a colourless syrup; this, after standing for some days over sulphuric acid in a vacuum, solidified to a hard cake of crystals. These were freed from a small quantity of oily mother-liquor by spreading out on a porous plate, and the acid was thus obtained quite colourless. After drying over sulphuric acid in a vacuum, it gave the following numbers on analysis:—

0·1334 gram substance gave 0·1070 gram H_2O and 0·2908 gram CO_2.

	Theory. $C_{10}H_{18}O_4$.		Found.	
C.....	59·41	per cent.	59·44	per cent.
H.....	8·91	„	8·91	„
O.....	31·68	„	31·65	„

Methylazelaic acid, thus prepared, melts at 43—44°, and when heated in small quantities in a test-tube appears to distil without decomposition. It is fairly easily soluble in boiling water, and, on cooling, the liquid becomes milky owing to the separation of the acid in oily drops. It is readily soluble in ether, alcohol, benzene, and chloroform, but cannot be recrystallised from any of these solvents, as on evaporating its solutions it is invariably obtained as a syrup which only crystallises again after standing for some time over sulphuric acid in a vacuum.

Methylazelaic acid is isomeric with sebacic acid (m. p. 197°) and heptylmalonic acid (m. p. 97—98°).

Salts of Methylazelaic Acid.

Silver Salt.—To prepare this salt, the pure acid was dissolved in a little dilute ammonia, the solution allowed to stand over sulphuric acid in a vacuum till free from excess of ammonia, and the silver salt precipitated by the addition of nitrate of silver. It is thus obtained as a white amorphous mass, which after collecting on a filter, washing

well with water, and drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0·2380 gram substance gave 0·0833 gram H_2O, 0·2507 gram CO_2, and 0·1233 gram Ag.

	Theory. $C_{10}H_{16}O_4Ag_2$.	Found.
C.....	28·84 per cent.	28·80 per cent.
H.....	3·84 „	3·89 „
Ag	51·92 „	51·80 „
O.....	15·38 „	15·51 „

If a neutral solution of the ammonium salt be treated with various reagents, it behaves in the following way:—

Calcic Chloride....	Added to a cold strong solution of the ammonium salt gives no precipitate; on warming however the calcium salt separates as a white curdy precipitate which when examined under the microscope presents very much the appearance of potato-starch.
Cupric Sulphate ..	Gives a bluish-green precipitate almost insoluble in water.
Lead Acetate	A white amorphous precipitate.
Zinc Sulphate	Gives no precipitate even in strong solutions. On warming, however, the zinc salt separates as a curdy-white mass.
Baric Chloride....	Gives no precipitate. The free acid dissolves readily in baryta-water, forming an easily soluble salt, not precipitated by boiling.
Magnesic Sulphate	Gives no precipitate.
Cobalt Nitrate....	Gives no precipitate in the cold; on gently warming the solution, a pink precipitate separates, which on boiling becomes reddish-violet.
Nickel Sulphate ..	When added to a hot strong solution produces a pale-green (almost white) precipitate.

Action of Bromine on the Disodium Compound of Ethylic Isoheptane-tetracarboxylate.

This experiment, which was instituted in the hope of obtaining a neptamethylene-derivative, as mentioned in the introduction, was carried out in the following way, and with the following quantities:—

	Expt. I.		Expt. II.	
Ethylic isoheptanetetracarboxylate	17·00	grams.	22·78	grams.
Sodium	1·93	„	2·60	„
Bromine	6·72	„	9·00	„

In both experiments, the sodium was dissolved in as little absolute alcohol as possible, the resulting sodic ethylate diluted with a large quantity of pure dry ether (about 100 c.c. in Experiment I and 200 c.c. in Experiment II), and mixed with the ethylic isoheptanetetracarboxylate. This caused the formation of a small amount of a yellowish flocculent precipitate, but the greater part of the disodium compound remained in solution. This mixture was cooled with ice, and the bromine added to it drop by drop, the whole being well agitated during the operation.

The resulting colourless product was then well washed with water, the ethereal solution evaporated, and the residual oil (which in Experiment II weighed nearly 22 grams) hydrolysed by boiling with a solution of potash in methyl alcohol. As soon as the hydrolysis was complete, the alcohol was distilled off, water added, the solution acidified with dilute sulphuric acid, and several times extracted with ether. After drying over calcic chloride and evaporating off the ether, a thick, almost colourless syrup remained, which was now heated to 200° to cause the tetracarboxylic acid to split up into dicarboxylic acid and carbonic anhydride. The residue, which was slightly brownish, was then converted into its ethylic salt by treatment with ethyl alcohol and hydrogen chloride. In this way, a brownish oil was obtained which on fractioning under reduced pressure (100 mm.) distilled for the most part between 200° and 260°, leaving a small quantity of a dark brown residue. On repeated fractioning, rather more than one-half of this oil distilled between 210° and 220°.

This oil was not analysed, but at once hydrolysed and the free acid examined. The whole quantity was boiled with a solution of potash in methyl alcohol for four hours, and the acid isolated in the usual way by acidifying with dilute sulphuric acid and extracting with pure ether. In this way, a considerable quantity of a nearly colourless syrup was obtained, which on standing for some days over sulphuric acid in a vacuum, solidified almost completely. The cake of crystals was purified from a little oily mother-liquor by spreading out on a porous plate, and after a few days became perfectly hard and colourless. This substance on examination proved to be methylazelaic acid. It melted at 43—44°, showed all the properties of this acid, and gave the following results on analysis :—

0·1351 gram substance gave 0·1075 gram H_2O and 0·2935 gram CO_2.

	Theory. $C_{10}H_{18}O_4$.	Found.
C	59·41 per cent.	59·25 per cent.
H	8·91 „	8·84 „
O	31·68 „	31·91 „

If methylheptamethylenecarboxylic acid had been present in the product of these reactions it would, on etherification with alcohol and hydrogen chloride, as described above, have yielded an ethereal salt, the boiling point of which would not have differed very much from that of ethylic methylazelate. By the hydrolysis of the fraction of this ethereal salt boiling at 210—220°, methylazelaic acid was obtained, but as far as we could see no trace of any other acid was present.

In order, however, to be more sure of this result, the higher and lower fractions of this ethereal salt (200—260°) were also submitted to hydrolysis, and in this way a syrupy acid was obtained, which on standing deposited a small quantity of methylazelaic acid. The mother-liquors from the crystals were now heated in a metal-bath for some time at 250—280° in the hope that if any methylheptamethylenedicarboxylic acid were present it would in this way be converted into its anhydride. On treating the product with dilute ammonia, however, it readily dissolved, showing that no such change had taken place.

From these results, therefore, it is evident that the action of bromine on the disodium compound of ethylic isoheptanetetracarboxylate no heptamethylene-derivative is formed.

XXII.—*On the Range of Molecular Forces.*

By A. W. Rücker, M.A., F.R.S.

The subject on which I have been asked to address the Chemical Society is the Range of Molecular Forces, and it will perhaps be well that I should, by way of prelude, explain the meaning which I myself attach to that term.

The investigation of the movements of a group of atoms or molecules is—though far more complex—in some respects similar to the study of the solar system. Newton proved that the Sun, the

planets, and their satellites behave as if a mutual action at a distance taking place between them modified their motions in accordance with a very simple rule. The wonderful impetus which this rule—the law of gravitation—gave to astronomy has led to many attempts to apply a similar method to molecular dynamics. Newton's law is thus frequently regarded as being only the first term of a more complex expression which, if complete, would—on the hypothesis of action at a distance—give the true law of mutual force between the ultimate particles of matter. The first term expresses all the results of experiment when the distances between the particles are considerable, but is insufficient when they are near together. The investigation of the other terms, which then become important, may be properly spoken of as the study of molecular forces.

Sir William Thomson (*Proc. Roy. Institution*, **11**, Pt. III, 483) has indeed expressed the opinion that it is possible that the phenomena of cohesion and others which are ordinarily ascribed to a departure at small distances from the law of gravitation, may not be inconsistent with it. In that case the additional terms are introduced by the attempt to apply a formula founded on the assumed continuity of matter to phenomena which are caused by its "coarse grainedness." Interesting as this suggestion is, it has not been worked out sufficiently to make it easy to translate all that we know of molecular action into language consistent with it. I shall, therefore, adhere to the ordinary usage, and assume that it is probable that a somewhat complex expression is required for the full statement of the law of force between two molecules.

If this formula were fully known, the physical interpretation to be given to it would still be open to discussion. Formerly it would no doubt have been considered sufficient to state as an ultimate fact that the law of the force in play between two molecules varies with the distance, that it is, for instance, attractive when they are far apart, repulsive when they are near together. Now, such a supposition is branded as artificial, but I venture to think that the artificiality is due rather to the acceptance of the hypothesis of action at a distance than to the assumed complication of the law. There are two closely related yet really distinct ways in which an apparent repulsive force may be (in the ordinary sense of the word) explained. It may, as has been the case with centrifugal force, be shown to be an effect of motion and inertia without any abandonment of the theory of action at a distance in the case of the other forces involved. Or it may be explained as a result of the properties of a medium by which matter is surrounded, or of which each atom is a specialised part. If action at a distance is thus reduced to action in proximity, if machinery is imagined adequate to account for the effects which distant bodies

produce upon each other, it should explain not only the repulsions but also the attractions, not only molecular elasticity but gravitation.

It is, I believe, sometimes thought* that the next step in the progress of the theory of the constitution of matter will be the assumption of an unexplained attraction only between its ultimate particles, while their elasticity is otherwise accounted for. This explanation of elasticity may or may not involve the hypothesis of a medium extending between the molecules.

If we dispense with it, we must not be content with vague analogies to account for the behaviour of two molecules during an encounter. It is true that a comet coming out of space toward the solar system might and probably would travel round the Sun without a collision, but in meteor swarms and in gases with non-repelling molecules collisions must take place, and Sir William Thomson (*Rep. Brit. Assoc.*, 1884, 616) has insisted on the fact that the result of such collisions in a gas must be the transformation of energy of translation into energy of vibration, with the spontaneous cooling of the gas as a result. It is precisely because no such effect is observed that the theory of elastic molecules is abandoned.

We are thus driven to suppose that elasticity is due to a repulsion, and, if we refuse to accept the theory of action at a distance, to introduce a medium by which the effect of a repulsion acting at a distance may be produced. It is, however, absurd to accept attraction at a distance, and to refuse to conceive of a repulsion acting under similar circumstances, to admit the one without explanation, and to invent a medium to account for the other. The most pregnant suggestions as to the constitution of matter which have hitherto been made do not proceed on these lines. An unexplained attraction is not assumed between vortex atoms in addition to the effects which follow from the laws of hydrodynamics. If it were necessary to adopt such an hypothesis, the vortex atom theory would evidently be as artificial as that embodied in the bald statement that the law of force changes with the distance from attraction to repulsion. It is perhaps possible that some such hybrid theory might serve as a useful basis for calculation, but from the philosophical standpoint it would not be a whit more conceivable than any other which involves action at a distance. If then we are to retain the language of the latter theory in any part of our discussion, it will be convenient and not less accurate to retain it throughout, on the distinct understanding that it is a conventional mode of representing facts which we do not fully understand, and which it does not suffice to explain completely.

* "On the Law of Molecular Force," by W. Sutherland, *Phil. Mag.*, July, 1887, p. 127.

A better method of expression may be found when suggestions like the vortex-atom theory of Sir William Thomson and the granular theory of Professor Osborne Reynolds (*Phil. Mag.*, December, 1885) are worked out. They, no doubt, will present grave difficulties as to the true nature of the action in proximity which takes place between contiguous granules, or between neighbouring layers of the ideal fluid in which the vortices are formed, but they will be justified as working hypotheses if they reduce the difficulties connected with the explanation of a large number of physical phenomena under a few heads.

If, then, we use provisionally the language of action at a distance in the expectation that it will ultimately be replaced by a theory of action in proximity, I think we ought, from the first, to admit that the law of force between molecules may be very complicated. We must not dismiss any idea which experiment suggests—such, for instance, as that there are several alternations of attraction and repulsion between two molecules as the distance between them diminishes—merely because it appears arbitrary and lacking in simplicity. It may be admitted, for the sake of argument, that we naturally look for simplicity in our fundamental assumptions, but if the machinery by which distant bodies affect each other, if the medium by which force is transmitted is simple, it by no means follows that its effects on matter can be expressed on the action at a distance hypothesis by an easy formula. Even in the case of a single ball moving through a perfect liquid bounded by an infinite plane, it will be apparently attracted to or repelled by the boundary according as it is projected parallel to or towards it. In the vortex-atom theory, the behaviour of two molecules during an encounter would depend entirely upon the circumstances of the collision, and cannot be very shortly described. In the important case of a single vortex ring passing by a large number of others uniformly distributed, it will experience a repulsion.* In Professor Osborne Reynolds's granular theory two molecules would exhibit mutual attraction and repulsion at different distances. In none of these cases can the fundamental assumptions be regarded as complicated, yet they all give rise to repulsions as well as attractions. They do not lead to simple expressions for the forces in play between molecules separated by distances of the same order of magnitude as their diameters. It would be perhaps too much to say that a simple result could only be produced by a medium of complicated constitution, but it is certainly true that we have *à priori* no more right to expect simplicity in the results of its action than simplicity in its constitution, and that the two are not necessarily obtained together.

* "Motion of Vortex Rings," J. J. Thomson. Macmillan, 1883, p. 55.

Thus much it has been needful to say in order to explain the point of view from which I wish to regard molecular forces in this lecture. I shall use the language of the action at a distance theory throughout, not—as I hope I have made clear—because I believe in it, but because, in so far as it can express them at all, it affords a self-consistent method of describing facts, the causes of which are as yet imperfectly understood. I shall not discuss the question of the representation of the forces by an algebraical formula. I cannot in the short time at my disposal exhaust the more limited subject to which I intend to confine myself. I desire only to lay before you an outline of the results of the principal experiments which have been made with the view of determining the distances through which a law of force apparently different from that of gravitation obtains. The greatest distance from a molecule at which this deviation is sensible is called "the radius of molecular action." It constitutes the superior limit to the range of molecular forces. The inferior limit is what is ordinarily called the radius of a molecule, but which, if we regard the molecules as exercising, when in close proximity, a mutual repulsion, is a length related to half the average minimum distance between their centres during an encounter.

This distance may depend on the temperature and on the physical state of the body, so that the diameter of a molecule may be different according as it is determined from experiments on gases or liquids. While retaining it as a convenient phrase, it will emphasise the conventional sense in which it is used if we speak of the diameter of a gaseous or liquid molecule as the case may be.

Between the limits thus defined, the law of force is unknown, though interesting suggestions have been made by Maxwell and others, but apart from this question, which, as I have said, I do not now discuss, the limits themselves may be determined very differently by different methods. The question as to whether a molecular force is "sensible" at a given distance from the molecule, depends partly upon the sensitiveness of the means used to detect it, and partly upon the nature of the phenomenon—electrical, optical, or otherwise—studied. It is impossible, therefore, to group the results of various observations into a connected whole, but it may nevertheless be useful to give a short *résumé* of the conclusions to which different observers have been led, and to attempt to arrange them, as far as may be, in order.

The largest values which have been obtained for the magnitude of the radius of molecular action have been deduced from observations on the condensation of films of gases and vapours on the surfaces of solids. Quincke (*Pogg. Ann.*, **108**, 326, 1859) in 1859 argued that if it be assumed that the law of molecular force is the same

for molecules in the gaseous, liquid, and solid states, the superior specific gravity of a solid would enable it to condense a gas upon its surface.

It is evident, however, from recent observations, that the nature of the solid is of even greater importance than its density. Among the more remarkable investigations on this point is that of Bunsen (*Wied. Ann.*, **20**, 552, 1883). A bundle of glass threads, the total surface of which was determined by preliminary observations and calculations, was enclosed in a chamber connected with a long tube, the lower end of which was dipped in mercury. The gradual rise of the mercurial column showed that an apparent absorption of carbonic acid by the glass was still going on at the end of three years. Later observations (*Wied. Ann.*, **24**, 1885, 322) proved that although the glass had been carefully dried, it is impossible to get rid of all the adhering moisture, unless the temperature is raised to a point not far short of the critical temperature of water. If this precaution has been omitted, carbonic acid, if present, will, according to Bunsen, be dissolved in the water-film, and since the inner layers of the liquid are subjected by molecular attraction to a pressure which is measured by hundreds of atmospheres, they are capable of absorbing enormous quantities of the gas. The strong acid thus formed appears to attack the glass, and it was found that nearly 6 per cent. of the total mass of glass threads employed had been disintegrated (*Wied. Ann.*, **29**, 1886, 161). The long-continued apparent condensation was, therefore, really slow chemical action. Nay, more, when the glass had been dried at a high temperature, no appreciable condensation of carbonic acid on the surface took place in eight days (*Wied. Ann.*, **24**, 1885, 335). A small quantity of water was then introduced and absorbed by the glass threads with a rapidity which showed that when really dry they acted as a more powerful desiccator than calcium chloride. Immediately after the introduction of the water the absorption of the CO_2 began as before, which proved that moisture was necessary to produce the phenomenon, or that carbonic acid does not condense to a measurable amount on dry glass.

By exposing glass threads to a series of constant temperatures until in each case no more moisture could be extracted by the passage of a current of dry air over them, and by measuring the successive quantities of water thus obtained, Bunsen was able to calculate the total thickness of the water film, which at each of these temperatures is irremovable by dry air. Under ordinary conditions water does not evaporate when its vapour exerts upon the surface a particular pressure, the magnitude of which varies with the temperature. Any internal layer parallel to the surface is subjected to an additional molecular pressure which increases rapidly with the depth, until the

boundary of the superficial portion of the liquid is reached, after which it becomes constant throughout the interior.

If the interior mass of water be replaced by a solid which exerts, *cæteris paribus*, a greater attraction on water than that of water itself, the molecular pressure would be increased, and thus the vapour-tension might be diminished without evaporation taking place. The defect of the external pressure would be balanced by the increased molecular attraction. If then we assume that the thickness of the water film which cannot at any given temperature be removed by dry air, is such that the pressure due to molecular attraction at the surface of the film is equal to the pressure of aqueous vapour at the temperature at which the experiment is made, it is possible, when the vapour-tension is known, to calculate the molecular pressure for given thicknesses of the film. The following table expresses Bunsen's results. The temperature is expressed in degrees centigrade. The thickness, neglecting some minor corrections, is indicated by D, and expressed in terms of micromillimetres ($\mu.\mu.$)* The pressure is expressed in atmospheres:—

$t.$	D.	$p.$
23°	10·52	0·027
107	6·70	1·278
215	5·47	20·791
329	3·63	—
415	1·32	—
468	0·42	—
503	0·00	—

If the desiccation with dry air was incomplete, the thickness of the films very much exceeded the above limits. Thus in one experiment in which the drying was purposely imperfect, the water layer was 232·4 $\mu.\mu.$ thick. The interpretation to be placed on these results has, however, been again rendered doubtful by the experiments of Warburg and Ihmori (*Wied. Ann.*, **27**, 481, 1886). These observers constructed a small balance of extraordinary delicacy, which was enclosed in an exhausted receiver, which could be connected at pleasure with vessels containing strong sulphuric acid or water. When it had been dried by frequent evacuation, water vapour was admitted, and the weight of the films deposited on a thin glass bulb suspended from the balance was determined.

They found that if the glass was washed with boiling water before the experiment, the deposited film was very much thinner than if this

* The micromillimetre is the millionth part of a millimetre.

precaution had been omitted. The thickness diminished in two experiments in the proportion of 48 to 4 and 23 to 2. In a third case, no film could be detected even when the temperature of the receiver was only 0·2° above the dew point.

Glass rods which have been boiled for a few minutes will not discharge an electroscope, even when they have for long been in a relatively damp atmosphere, under circumstances such that rods of the same glass which have not been similarly treated conduct readily.

The film of moisture adherent to glass may thus be divided into two parts, distinguished as the permanent and temporary respectively, of which the latter disappears under the influence of a long-continued current of dry air, while the former can only be removed by raising the temperature. Warburg and Ihmori conclude that the temporary film (with which they alone deal) is not produced by the molecular attraction of the glass as a whole on water vapour. They refer to experiments which prove that if glass powder be boiled in water measurable quantities of alkali are dissolved. They, therefore, assume that there is a certain quantity of free or loosely combined alkali on the surface of the glass, and that it absorbs water until a solution is formed, the vapour-tension of which corresponds to the hygrometric state of the air in the neighbourhood. If carbonic acid is then absorbed by the solution, the glass may be attacked, and the process continued.

Further experiments have been made by Ihmori (*Wied. Ann.*, **31**, 1006, 1887). He finds that the water films on clean unvarnished metal surfaces are extremely thin, varying from 10 to 3 $\mu.\mu.$ On oxidised metal, they may be twice as thick, and he inclines to the view that in all cases the phenomenon is due to oxidation. Varnished metal may in $20^{m.}$ absorb enough to produce a layer 286 $\mu.\mu.$ thick, and sealing-wax also absorbs large quantities. Nineteen experiments on quartz gave a mean thickness of 22 $\mu.\mu.$, with a maximum of 62 $\mu.\mu.$ Six observations made when the crystal had been previously washed gave a mean of 4 $\mu.\mu.$ and a maximum of 6 $\mu.\mu.$ only. The mean result of 11 experiments on platinum was under 3 $\mu.\mu.$, the maximum being 12·2 $\mu.\mu.$ In the case of a piece which was specially cleaned by heating, no condensation could be detected. Agate absorbs large quantities of water. Films, the thickness of which varied between 562 and 1640 $\mu.\mu.$, are stated to be the result of an hour's exposure to a moist atmosphere. It is, however, well known, though Herr Ihmori does not refer to the fact, that agate consists of alternate layers of quartz and a porous form of silica allied to opal. Professor Judd has kindly furnished me with specimens which have been immersed in coloured solutions. These have been absorbed by the porous

layers, and thus coloured bands are formed. In this way a good imitation of an onyx may be produced. There can be no doubt that the surface exposed by the agate to the water-vapour includes that of the interior of a vast number of capillary tubes, and is enormously greater than the mere external surface. The quantity of water absorbed does not, therefore, give any indication of the thickness of the water film, and no deduction as to the radius of molecular action can be drawn from it.

The net result of these experiments is to render it doubtful whether in the case of substances which are not dissolved or chemically acted on by water, any measurable temporary film is formed at temperatures above the dew point. If such a film is formed in these cases, its thickness is, according to Warburg and Ihmori, in general very much less than the radius of molecular action as determined by Quincke.

Pfeiffer (*Wied. Bei.*, **8**, 635, 1884), who published some experiments on the absorption of gases by solids at high pressures, arrived at the conclusion that layers of ammonia and carbonic acid, of the thickness of 450 $\mu\mu$. and 240 $\mu\mu$., are formed on charcoal made from firwood. As, however, the result is based on calculations made from boxwood charcoal, in which it is assumed that it condenses SO_2 exactly in the same way as glass does, but little reliance can be placed on it. It is probable that water films play as important a part in the apparent condensation of SO_2 on the surface of glass as they do in that of CO_2.

Another group of experiments has been made with iron oxide, alumina, and silica, which readily absorb water and carbon bisulphide. Thus Müller-Erzbach (*Exner's Rep.*, **21**, 409, 1885) measured the grains of finely powdered oxide of iron under the microscope, and concluded that a certain area was greater than that of a given weight of the powder. He then deduced from this datum and the weight of CS_2 absorbed by the oxide the thickness of the film. Assuming that the specific gravity of the absorbed CS_2 was increased from 1·27 to 1·60, by causes similar to those which affect the specific gravity of water of crystallisation, he concluded that the film was at least 1000 $\mu\mu$. in thickness. Similar calculations (*Exner's Rep.*, **21**, 553, 1885) gave 1700 $\mu\mu$. for the thickness of a film of CS_2 adherent to alumina. He finally concludes that the radius of molecular action is at least 1500 $\mu\mu$. (*Wied. Ann.*, **28**, 696, 1886). Kayser (*Wied. Ann.*, **14**, 450, 1881), as the result of experiments on the condensation of gases on glass thread, was of opinion that the quantity condensed depended on the closeness with which the fibres were packed, and that the radius of molecular action was of the same order of magnitude as the diameter of the threads. He fixes its magnitude at from 2000 to 3000 $\mu\mu$. As these observations were made before the importance of getting rid of the water film by

heating had been demonstrated, they cannot be accepted as supporting this enormous value.

Passing next to the condensation of the more permanent gases, I may refer to a calculation made by Callendar,* on the assumption that the differences between the coefficients of expansion of air between 0° and 100° C., given by various air thermometers, depend on the quantity of air condensed, when they are cooled, and thus upon the ratio between the surface and volume of the bulbs, which of course varies with their shapes. He shows that the values for the coefficients of expansion of air at constant volume between 0° and 100° C. obtained by Regnault, Balfour Stewart, and himself, would agree if the weight of air condensed between those temperatures is 10^{-6} grams per sq. cm. From this we deduce that the thickness of the film removed by heating from 0° to 100° C. would be 10 $\mu.\mu.$, if the density be assumed to be the same as that of water. Schumann (*Wied. Ann.*, **27**, 91, 1886) has also recently pointed out that if the layer of air condensed on glass reaches considerable dimensions, the length of a mercurial thread in a capillary tube would be appreciably different, according as the film was or was not present. He therefore connected a long bent capillary tube with a bulb, and when the positions of the ends of a thread of mercury had been determined it was transferred to the bulb. The tube was then exhausted and heated to 312° C., which could be accomplished without heating the mercury. When the apparatus had become cold, the mercury was returned to the capillary tube. Its length was found to be precisely the same as before. The thickness of the air film removed by the heating could not, therefore, according to Schumann, have been greater than 70 $\mu.\mu.$ His method of course involves the assumption, which seems legitimate, that the mercury would not remove the film from the glass as it moved along the tube.

An argument to the same effect may be drawn from some observations made by Bottomley (*Chem. News*, **51**, 85, 1885), and published in 1885. He exhausted a vessel containing glass fibres by means of a mercury pump until the pressure as indicated by a McLeod gauge was 0·3 M.† He then heated the vessel and its contents until some of the glass fibres began to soften, and collected the gas which was given off. It amounted in all to 0·45 c.c., at 15° C. and 760 mm., and when analysed was found to contain 8·24 per cent. CO_2, 24·8 per cent. O_2, and 75·2 per cent. N_2. The total surface of the fibres was 14·48 sq. cm. The gas as it left the vessel was dried, and it is not stated that the

* "On the Practical Measurement of Temperature," *Phil. Trans.*, vol. 178 (1887), A., p. 161.

† M = 1 millionth of an atmosphere.

glass fibres had been previously washed, so that there probably was a water film of the magnitude of which no estimate could be formed. It is therefore probable that the gases were partly dissolved, but at all events the observations lent no support to the idea that the gas film on glass dried only by contact with dry air is very thick. If we assume that the mixture when collected was of the same density as air, and that when in contact with the glass it had the same density as water, the thickness of the film of condensed gas was $4\,\mu.\mu.$, which is somewhat less than the number deduced on the same hypothesis from Callendar's suggestion.

On the whole, looking only at the very contradictory results attained by different researches, and without regard to arguments which I shall presently adduce, I must confess that I do not think we can at present draw any certain conclusion as to the magnitude of the radius of molecular action from observations on the condensation of vapours or gases. To justify this view, I cannot perhaps do better than quote from two of the gentlemen who have studied the phenomena most closely.

In 1885, Müller-Erzbach remarks (*Exner's Rep.*, **21**, 1885, 407):—"Ich habe nun . . . ein Mittel gefunden, durch welches ich auf einfache Weise glaube beweisen zu können, dass die in Betracht kommenden Molecularkräfte nicht nur bei unmittelbarer Berührung wirksam sind, sondern selbst noch in einem grösseren Abstand als ihn Hr. Quincke nach seinen Versuchen bestimmt hat."

In 1886, Warburg and Ihmori sum up these results as follows (*Wied. Ann.* **27**, 507, 1886):—"Es liegt uns fern, die Richtigkeit der Schlüsse Quincke's anzuzweifeln . . . . Allein in den Messungen, welche wir über das Gewicht der Wasserhaut bei Glas und anderen Körpern angestellt haben, ist uns nichts entgegengetreten, woraus eine Wirking der Molecularkräfte auf messbare Distanzen hin zu erschliessen wäre."

The first important attempt to measure the radius of molecular action was made by Plateau (*Statique des Liquides*, 1873, **1**, 210). Arguing that the surface-tensions would decrease if the thickness of a soap film became less than twice the radius, he made experiments to determine whether the pressure exerted on the enclosed air depended on the thickness. His method was open to criticism. The soap bubble was made of a mixture of soap, water, and glycerine, and thus its constitution would alter unless it were surrounded by aqueous vapour of a determinate tension. No precautions were taken to secure this condition. The bubble was produced at the end of a tube bent so as to form a manometer. The liquid used to measure the pressure was water, while the rate of thinning of the bubble was accelerated by enclosing it in a covered

beaker in which were placed some sticks of caustic potash. Under these circumstances it is impossible to say what the final constitution of the liquid might be. By measuring the specific electrical resistance of various mixtures of glycerine and soap and water, and the resistance of cylindrical soap films formed of the same substances, Professor Reinold and I have been able to measure the changes in the constitution of films when subjected to variations in the temperature or hygrometric state of the surrounding air. We found it very difficult to secure constant conditions, and that under circumstances far more favourable than those of Plateau's experiments the films lost one of the 57·7 volumes of water originally contained in every 100 of solution in times which varied between four and eight minutes (*Phil. Trans.*, Part II, 1881, 486).

As Plateau's film lasted two days, it is evident a change of composition sufficient to have caused a marked or considerable change in surface-tension due to thinning might have occurred. Plateau observed no change in the pressure when the colours of the bubble proved that its thickness was 118 $\mu.\mu$, and thence concluded that the radius of molecular action is < 59 $\mu.\mu$. This inference is not so certain as he appears to have thought it to be. Maxwell (Art. "Capillary Action," *Enc. Brit.*, ed. ix) has shown that if we neglect the change of density in the surface of the liquid and the thermal phenomena which accompany the thinning of a film, the surface-tension will remain unchanged until the thickness is equal to the radius of molecular action. It is difficult to estimate the extent to which this result might be affected by a theory which took cognisance of the motion of molecules and the change of surface-density. Perhaps, therefore, all that we are entitled to say is that if no change is observed in the tension of a film of given thickness, the radius of molecular action must be less than that thickness, but that if a change is observed it must be greater than half that thickness. Thus the superior limit fixed by Plateau's experiment would be twice as great as it has been generally assumed to be.

Quincke (*Pogg. Ann.*, 1869, **137**, 402) attacked the problem in another way. He placed a layer of Martin's silvering solution between a glass cylinder of 120 mm. radius and a plane sheet of glass. A double wedge of silver, which was thinnest in the centre, was deposited on the surface. Two sheets of glass thus prepared were fastened together with a small interval between them, with their silver sides inwards, and adjusted so that silver layers of equal thickness were as nearly as possible opposite to each other. A glass cell, open at the top and bottom, having thus been formed, the lower part was immersed in distilled water. The cell being vertical the water rose highest in the centre, where it might be considered to be

in contact with the glass. On each side, as the silver sheet became thicker the capillary elevation diminished. It was measured at known distances from the centre, and the angle between the solid and the liquid surface calculated. This would become constant when the thickness of the silver layer was such that the attraction of the glass on the water was negligible. The silver was afterwards converted into iodide of silver, and the thickness of the layer at different parts deduced from the colour. Similar experiments were made with other substances. The results may be summed up as follows, if we write ρ for the radius of molecular action in terms of micromillimetres:—

$\rho > 54{\cdot}2$ for water, silver, and glass,
$= 43{\cdot}3$ „ mercury, sulphide of silver, and glass,
$= 59{\cdot}0$ „ mercury, iodide of silver, and glass,
$< 80{\cdot}0$ „ mercury, collodion, and glass.

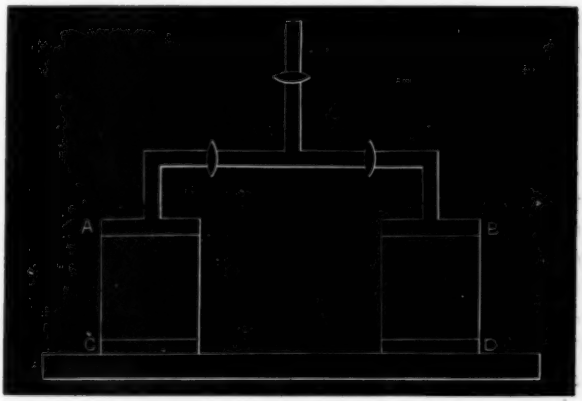
The quantity ρ as given by these experiments strictly speaking measures, not the radius of molecular action, but the distance at which the difference between the molecular forces exerted by glass and silver becomes inappreciable. This would probably be somewhat less than the true radius, but nevertheless the net result is to show that the radius of molecular action is approximately $= 50\ \mu.\mu$. It is much to be desired that this conclusion should be in every way tested, and that similar observations should be undertaken by other physicists. I hope to show in the course of this lecture that it does receive important confirmation from the behaviour of thinning soap films.

Plateau's experiment has been repeated and modified in various ways. Lüdtge (*Pogg. Ann.*, **139**, 1870, 620), instead of directly measuring the pressure exerted by bubbles, compared the pressures due to thick and thin films by balancing them against each other. A soap film having been formed at the end of a tube, it was allowed to thin, and the other end was then closed by another film. Air was forced in, the films assumed the form of spherical segments, and their curvatures were compared. If p is the pressure exerted by a soap bubble, of which T and R are the surface-tension and radius respectively, $p = 4T/R$. Hence if the tensions of the thick and thin films were different, their radii would be different also. He concluded that the radius of molecular action was much larger than Plateau and Quincke's observations would have led us to suppose, and that, contrary to expectation, the thicker film had the less surface-tension. His experiments were repeated and extended by Van der Mensbrugghe (*Bruxelles Acad. Sci. Bull.*, **30**, 1870, 322), who was unable to detect the alleged change of tension. Afterwards, however, he suggested and adduced experiments to prove that the phenomenon

was probably real, and due to the cold produced by the continual evolution of fresh liquid surfaces as the films thinned (*Bruxelles Acad. Sci. Mem.*, **43**, 1882, No. 4, 18).

Lastly, Professor Reinold and I (*Phil. Trans.*, **177**, Part II, 627, 1886) have employed similar methods.

We balanced two cylindrical films, the one against the other; one of them was kept thick by passing up it an electric current which we



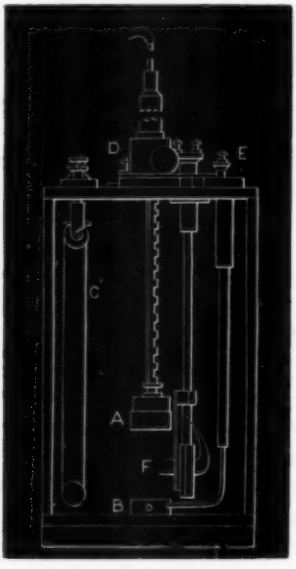
University of Michigan

have shown carries the matter of a thin film with it (*Phil. Mag.*, **19**, 94, 1885). The other was allowed to thin, and the tensions were deduced from the curvatures. The above figure represents diagrammatically the essential parts of the apparatus. The cylinders were formed between platinum rings, and their interiors could be put in connection with each other or with the external air by stopcocks. The apparatus actually used was somewhat complicated. The films were formed in a closed glass box surrounded by water. They could be made and adjusted without opening the box, so that the temperature and hygrometric state of the enclosed space were constant. A difference of surface-tension was indicated by a bulging of one film and a contraction of the other. Several possible causes of error were investigated, and as the distorted films were unduloids, formulæ were devised by means of which we could at once calculate the difference of the tensions of the two films when their lengths and maximum or minimum diameters were known. We found, as has indeed been noticed by others, that the surface-tension of a newly-formed film diminishes, and that from 10 to 15 minutes must elapse before it acquires an approximately constant value. By measuring the magnitude of the changes of surface-tension thus developed, we proved that they were far too great to be accounted for, as Van der Mensbrugghe supposed, by cooling due to thinning. The calculated

change was 0·0016 per cent., while we observed changes of 9 per cent. The effect is probably only a striking instance of the difficulty of preserving a liquid surface pure.

If, however, two films of very different thicknesses, but neither of which had been very recently formed were compared, the difference of tension (if any) was very small, and was not constant either as to sign or amount. We concluded that no evidence of a change in surface-tension dependent on the thickness of the film is furnished by a direct comparison of the tensions of thin and thick films over a range of thickness extending from 1350 millionths of a millimetre down to the stage of extreme tenuity when the film shows the black of the first order of Newton's scale of colours. Had any such difference as large as one-half per cent. of the value of the tension existed we must have detected it.

The magnitude of the lower limit when the film appears black was given by the results of a previous research (*Phil. Trans.*, Part II, 1883, 645). We had determined the thickness of black soap-films by measurements based on two independent methods, the one electrical, the other optical. In the first we measured the resistance of cylindrical films and deduced the thickness on the assumption that the specific resistance was the same as that of a thick layer of the same liquid.



The apparatus used is shown in the figure. The film was formed between the platinum rings A and B. The lower part of the glass

vessel was flooded with the solution, and C is an endless linen band which dipped in the liquid, and could be rotated from the outside. It was thus kept moist, and the hygrometric state of the air was maintained at a constant point. The current flowed from the binding screw D to A, thence through the film to B and E. At F a pair of insulated gold wires penetrated the film. They were connected with the opposite quadrants of an electrometer, and the differences of potential between them and between the extremities of a known resistance inserted in the circuit were measured alternately. From these, the resistance of the film between the needles was deduced.

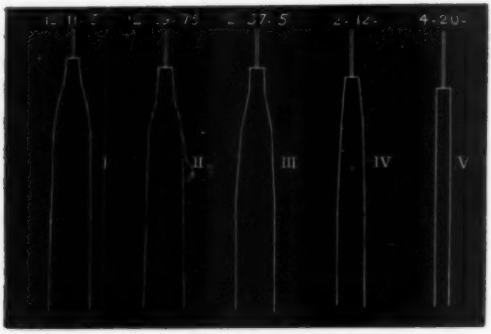
In the second method we passed the two rays of light, used in an apparatus* for the production of the phenomenon of interference by means of thick plates, through two tubes in which a number of plane films had been formed. A known number of films was then broken in each tube in turn. The thickness was deduced from the displacement of the interference bands on the assumption that the mean refractive index of the thin films was the same as that obtained by the ordinary methods from experiments on the liquid in mass. The results may be summarised as follows :—

Liquid.	Method.	No. of films observed.	Mean thickness in terms of 10^{-6} mm.	Probable error of a single observation.
Liquide glycérique	Electrical ..	5	11·9	± 0·2
" "	Optical	7	10·7	± 0·6
Soap solution, without glycerine	Electrical ..	13	11·7	± 1·4
	Optical	9	12·1	± 0·8

The close agreement between these numbers, obtained by different methods, and by calculations based upon different assumptions, proves conclusively that the thickness of a black film is generally about 12 $\mu.\mu$. We found that the thickness of different films might vary within several millionths of a millimetre, but that in any given film the thickness of the black part remains constant—at all events from a short time after its first formation. At first sight, then, it appears as though our result was in direct opposition to that obtained by Quincke, and proved that the radius of molecular action is <12 $\mu.\mu$. This is not the interpretation we ourselves put upon it. The black and coloured parts of a film are separated by a sharp line, which shows that there is a discontinuity in the thickness. Thus, in extreme cases, the rest of the film may be 250 times thicker than the black part with which it is apparently in contact.

* Sometimes called a Jamin's Interferential Refractometer.

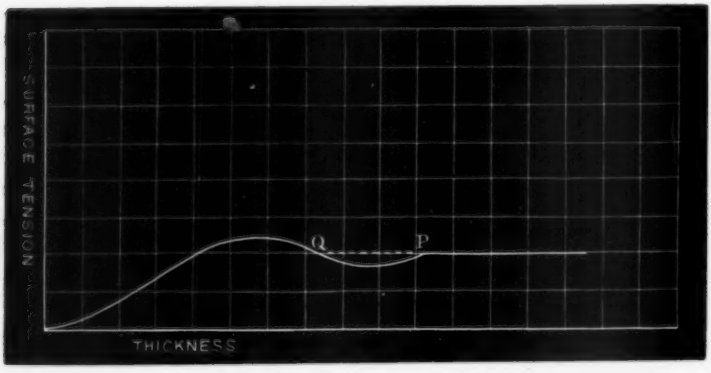
The accompanying figures represent the life history of a film which Professor Reinold and I watched for several hours. They are sections



deduced from the colours observed at intervals. The thickness is magnified 5000 times more than the length. The upper part of the film was black, and the enormously rapid change in thickness at the edge of the black is well shown.

Sir William Thomson (*Proc. Roy. Instit.*, **11**, Part III, 485, 1887) and Professor Reinold and myself (*Phil. Trans.*, **177**, Part II, 679 and 684, 1886) independently arrived at the conclusion that our observations on the uniform thickness of the black part of a film and on the discontinuity in the thickness at its edge prove that when the film reaches a certain degree of tenuity the surface-tension diminishes to a minimum, and begins to increase again when the thickness is somewhat greater than 12 $\mu.\mu$.

The relation between the surface-tension and thickness may thus be represented by a curve like that shown in the accompanying figure. When the thickness is great the surface-tension is constant. When it reaches the value which corresponds to P, the tension begins to



diminish. The thicker parts of the film now tear the thinner parts asunder. Rupture would inevitably follow were it not for the fact that when a certain degree of tenuity is reached the surface-tension again increases, and when the thickness is 12 $\mu.\mu.$ becomes equal to that of a thick film, as indicated by the equality of the ordinates at P and Q. Equilibrium is thus possible between two parts of a film of which the one has the thickness corresponding to Q, and the other any thickness greater than that corresponding to P. It is also stable, for any further decrease in the thickness of the film below Q would cause a further increase of tension; the thinner parts would therefore contract and become thicker. In other words the film could not, under ordinary circumstances, thin to below that thickness for which the surface-tension regains its normal value. The discontinuity at the edge of the black, and the uniform thickness of a black film, are thus both accounted for. Our failure to detect any measurable difference of surface-tension between thick and thin films means not that the radius of molecular action is less than 12 $\mu.\mu.$, but that the changes of tension which produce the sharp edge of the black are certainly $< 0{\cdot}5$ per cent. of its whole value.

Let us then examine this remarkable phenomenon a little more closely. It is a result of ordinary observation that in a thinning film there is a range of unstable thickness, which is always missing between the black and coloured parts. The instability is very strikingly shown by an experiment which Professor Reinold and I have often performed. If an electric current be sent up a cylindrical film, the upper part of which is black, the sharp edge is obliterated. The current carries liquid up with it, smoothes off the discontinuity, and the colours pass into the black by a gradual transition through grey.

As soon, however, as the current is broken, the old state of things is re-established. The grey disappears, and the black is again bounded by a definite sharp edge. The change takes place in from 10 to 16 seconds. The colours which thus vanish correspond to the range of unstable thickness. Its lower limit is fixed by the experiments of Professor Reinold and myself as being nearly 12 $\mu.\mu.$ The upper limit is more difficult to determine, as the colour by which the black part of the film is bordered varies, and is probably largely determined by accident. This, however, may certainly be said, that when the film thins in the normal way, the discontinuity in the thickness never occurs within the grey region. The colour next to the black may rise into the second or higher orders; it never sinks below a full white of the first order. It is, therefore, probable that the decrease in surface-tension begins at a thickness less than that which corresponds to the middle of the white, and greater than that which

corresponds to the beginning of the black or faint blue which surrounds it. According to Newton these thicknesses are 96 and 45 $\mu.\mu.$ respectively, the mean being 70 $\mu.\mu.$ Let us now assume that Quincke's value of the radius of molecular action is correct. The greatest possible thickness at which the surface-tension of a film could begin to diminish is then 100 $\mu.\mu.$ Any film thicker than this would have two complete surface layers, and a layer of "interior" liquid separating them. Its surface-tension could not therefore depend on the thickness. On the other hand, if Maxwell's theory were correct, the tension would remain unaltered until the thickness was equal to the radius of molecular action, that is, 50 $\mu.\mu.$ It is not, I think, probable that any improvement in the theory would reduce this limit, though it might increase it. Hence we arrive at the conclusion that *the limits of thickness fixed by observation as those between which the surface-tension of a film begins to diminish* (96 *and* 45 $\mu.\mu.$), *are practically identical with the limits deduced by theory from Quincke's experiment* (100 *and* 50 $\mu.\mu.$) *as those within which such decrease ought first to be observed.*

Curious and important as I venture to think this conclusion is, I do not wish to press it too far. The fact that the limits of doubt imposed by two independent lines of argument are at the present moment the same, is a more or less accidental coincidence. The vital point is that the value of the radius of molecular action as determined by Quincke, is certainly of the same order as, and cannot possibly differ much in magnitude from that which may be deduced from the properties of soap films. Quincke's result is, therefore, not an isolated fact. It receives the strongest possible confirmation from a totally different line of research. The matter may also be presented in another way. The radius of molecular action cannot, if Maxwell's theory be accepted, be greater than 96 $\mu.\mu.$, which is the superior limit to the thickness at which the surface-tension begins to decrease. If the ordinary view be correct, it cannot be less than one-half of 45 $\mu.\mu.$, which is the lower limit to that thickness.

Hence the true value of the radius of molecular action lies between 96 and 23 $\mu.\mu.$, and the value found by Quincke (50 $\mu.\mu.$) is intermediate between these.

However, therefore, we combine the figures, we deduce from the two observations the same result, viz., that 50 $\mu.\mu.$ is of the same order of magnitude as the radius of molecular action, a conclusion which it is not too much to say has now strong claims to rank as an ascertained fact.

Van der Waals* deduced from his theory distances between 0·15 and

* "Die Continuität des gasförmigen und flüssigen Zustandes." Van der Waals. Translated by F. Roth. Leipzig, 1881, p. 107.

0·29 $\mu\mu$., which are less, but as he thinks not very much less, than the radius of molecular action, and he expresses the opinion that Quincke's value is larger than our knowledge of capillary phenomena will allow. As the numbers he himself obtains are from 0·01 to 0·02 of the thickness of a black soap-film, it is evident from the above discussion that they are very much too small.

Passing next to the lower limit of the unstable thickness (12 $\mu\mu$.), we must enquire what is the cause of the increase of surface-tension to which the uniform thickness of the black film is due. On this point it may be well to speak with a certain amount of reserve until the theory of the constitution of liquids is more fully developed. If, however, we accept equations obtained by Maxwell, in which the movements of the molecules and the surface change of density are neglected, the phenomenon can be at once explained, if we suppose that the increase of surface-tension corresponds to a change from attraction to repulsion in the intermolecular forces. If the force exerted by a liquid mass on a particle is repulsive when the distance of the particle from the surface lies between certain limits, then the tension of films, the thickness of which is comprised between the same limits, will increase instead of decreasing as the thickness diminishes. From this point of view, therefore, the explanation of the sharp edge of the black part of a soap film would be that when the molecular force between a liquid bounded by a plane surface and a molecule in its neighbourhood first becomes sensible, it is an attraction, but that at some lesser distance, which is nevertheless greater than 12×10^{-6} mm., it becomes a repulsion. It must, however, be distinctly understood that the explanation that the increase in surface-tension is due to the action of a repulsive force is only put forward as suggested by Maxwell's theory. I think that this conclusion is very much more doubtful than that which determines the thickness at which the surface-tension would begin to diminish, but the further discussion of this point would involve a mathematical argument with which I will not at present trouble you.

If, however, apart from the question as to how it may be mechanically explained, the view be accepted that the surface-tension falls to a minimum and is again increasing when the thickness is 12 $\mu\mu$., the very interesting question arises whether there is any experimental evidence that at some thickness less than 12 $\mu\mu$. it again diminishes.

In answer it may be remarked that in general the black spreads slowly and quietly over the film, and may take an hour or more in travelling from the top to the bottom of a cylindrical film 26 mm. long. All the statements I have hitherto made refer to cases in which the mode of formation was thus normal (*Phil. Trans.*, **177** [2], 677, 1886). "At times, however, the black is formed with something like a

convulsion. Not only does it spread with extraordinary rapidity, but the edge is violently disturbed, and large patches rise through the coloured part of the film. Whenever this occurs the film breaks before long, but in four cases we were able to obtain measurements before rupture. We are not able to produce this phenomenon at will, but the few observations we have been able to make on it are in agreement among themselves." In all cases the cylinder which thinned most rapidly bulged, the other contracted. The differences thus produced between the diameters varied from 0·35 to 0·75 mm., and could not be accounted for by the sudden renewal of the surface of the thinning film (which would have produced a change in the other direction), or by any other cause known to us. The measurement of the thickness of such films would probably settle the question as to whether the black when formed in this abnormal way corresponds to the state of unstable equilibrium which would exist if, after increasing, the surface-tension again diminished as the film became thinner, or to a second state stable within narrow limits of thickness. Such experiments would, however, be attended with extraordinary difficulties, as they would involve measurements on films which are practically always short-lived, and which are possibly theoretically unstable.

Another method of investigating the magnitude of the radius of molecular action is based on the phenomenon of electrolytic polarisation. If we immerse in acidulated water two similar metal plates which are not attacked by the acid, they will be at the same potential. When a current is passed from the one to the other they will, if the metal and acid have been properly chosen, become covered with films of oxygen and hydrogen respectively. The sum of the differences of potential due to metal | gas | liquid, is not the same as that due to the single metal | liquid contact, and varies with the nature of the gas. Hence the coated plates assume different potentials, but the full difference is not established until the surface-density of the deposited gas exceeds a certain value. If then we suppose that the film is uniform, and that the metal and liquid cannot be regarded as completely separated until the thickness of the film exceeds the radius of molecular action, we may by plausible assumptions as to the density of the gas estimate its magnitude.

Thus F. Kohlrausch (*Pogg. Ann.*, **148**, 153, 1873) concluded that if the gases are supposed to be at their ordinary densities the polarisation of a platinum electrode is complete when it is coated with a layer of oxygen 20 $\mu.\mu.$ in thickness. It is evident that this assumption as to the density of the gas is totally at variance with the views ordinarily put forward in discussions on the condensation of gases on solids as to the great molecular pressure to which the condensed film

is subjected, and that doubt on this point deprives such observations of all value for our present purpose. To reduce the uncertainty as to the density of the polarising layer, it is evidently better to substitute another metal for a gas. This has recently been done by Oberbeck (*Wied. Ann.*, **31**, 337, 1887).

The films were deposited on platinum electrodes, and the liquids used were solutions of $ZnSO_4$, $CdSO_4$, and $CuSO_4$. Three platinum plates were immersed in the solution contained in a rectangular cell. Two plates of the metal of which the sulphate was used (zinc, say) were interposed between the central platinum plate and the other two, and were used as electrodes by means of which a layer of zinc was deposited on both sides of the central plate. Electrolysis was continued until the difference of potential between the coated plate and the external platinums, which were not affected by the current, was the same as that between Zn and Pt (1·13 Daniell). The current was then stopped, and for a time the electromotive force slowly diminished, after which a very rapid decrease was observed. The film was spontaneously re-dissolved, and the sudden change in the rate of the fall of the electromotive force was regarded as indicating that the thickness of the metallic layer had become less than the radius of molecular action.

If a is the quantity of metal deposited on each sq. cm. (which could be calculated from the current strength, &c.); and
θ the time which elapsed after the completion of the electrolysis before the rapid fall of E.M.F.,

it was found that these quantities were connected by a relation of the form—

$$a = A + B\theta,$$

where A and B are constants.

Of these, A is the quantity of zinc on each sq. cm., when its thickness is just less than the radius of molecular action, and by means of two experiments in which a and θ have different values, it can be calculated. Oberbeck concludes that if the specific gravities of the electrolytic layers are the same as those of the metals under ordinary circumstances, the thicknesses necessary to establish the full difference of potential are between 2 and 3 $\mu.\mu.$ for zinc, between 1 and 2 $\mu.\mu.$ for cadmium, and rather less than 1 $\mu.\mu.$ for copper.

Interesting as these results are, they are, as Oberbeck himself points out, open to criticism. The rapid decrease in the E.M.F. might be explained by supposing that when the zinc layer becomes very thin, parts of the platinum plate are uncovered, and that local action takes place which rapidly dissolves the zinc. This is certain to occur unless

the metallic film is uniform. To test its uniformity, the experiment was repeated with a solution of acetate of lead as the electrolytic liquid. The colour of the platinum electrode showed that the deposit was uniform over the greater part of the plate, but was slightly thicker towards the edges. No data as to the colours displayed are given, but unless the difference of the tints was very slight, it would correspond to a variation of thickness greater than that assigned to the radius of molecular action.

The next method which I propose to describe aims at a measurement of the distance between two consecutive layers of molecules. If plates of Zn and Cu are connected by a metallic wire, they assume different potentials (P and p), the Zn becomes positively the Cu negatively electrified. When the plates are parallel to each other, and separated by a distance t centimetres, they form a condenser, and if $+e$ is the charge upon 1 sq. cm. of the Zn plate $e = (P - p)/4\pi t$.

Hence et is a constant which depends only on the nature of the metals and is independent of the distance between them. When the metals are in contact, the potential difference remains unaltered, and we may regard the surface molecules as being oppositely charged and separated by a very small interval. The two charges are said by v. Helmholtz to constitute an *electric double layer* (*Pogg. Ann.*, **89**, 211, 1853; *Wied. Ann.*, **7**, 337, 1879).

The mutual action of two metals, or of a metal and liquid when in contact, is therefore the resultant of the molecular forces and the electrical attractions and repulsions which are in play between the different parts of the double layer.

Thus v. Helmholtz (*Berlin Wissenschaft. Abh.*, 925, 1882; see also *Wied. Ann.*, **16**, 31, 1882) has proved theoretically that the surface-tension depends on the electrical charge, and is a maximum when it vanishes, and, as is well known, Lippmann (*Annales de Chemie*, **5**, 494, 1875) has shown that the surface-tension of mercury in contact with dilute acid is a function of the difference of potential between them, and that every motion of the common surface changes the potential difference in such a way as to produce an alteration in the surface-tension which checks the motion. By means of a theory which it is unnecessary to reproduce here, he (*Compt. rend.*, **95**, 687, 1882) drew from his experiments the conclusion that for such differences of potential as he employed the capacity of a given area of a Hg | H_2O surface is constant. Hence the distance between the two electrified surfaces is constant and can be deduced from the theory. The value found is 0·03 $\mu.\mu$. Oberbeck (*Wied. Ann.*, **21**, 157, 1884) and Falck have measured the electromotive force of polarisation produced by alternating currents on metals immersed in solutions of K_2SO_4, KCl, KBr, and KI. They

conclude that the capacity of the double layer is not constant, but is a function of the charge, so that its thickness must be regarded as variable. They deduce, however, its limiting value when the charge is zero, *i.e.*, the distance between the nearest layers of molecules under normal conditions when no current is passing. The magnitude of this initial value depends more on the metal than on the liquid. The following table holds for solutions of KCl or KBr, and gives the thickness of the double layer deduced from the formula—

$$t = 1/4\pi C,$$

where C is the initial capacity.

Metal.	t in terms of 1 $\mu.\mu.$
Nickel	1·04
Aluminum	0·67
Gold	0·06
Silver	0·02

When dimensions so small as these are reached, the validity of the method of representing the phenomenon as due to two uniform layers of electricity is very doubtful. The values of t in the case of gold and silver are comparable with the diameters of the molecules themselves, and thus t can only be regarded as a conventional length representing the thickness of an artificial condenser by which the real molecular arrangements may be approximately imitated.

L. Lorenz (*Pogg. Ann.*, **140**, 644, 1870) has also based upon electrical theory an estimate of the distance between neighbouring water molecules. He concludes that it is $< 0{\cdot}1$ $\mu.\mu.$

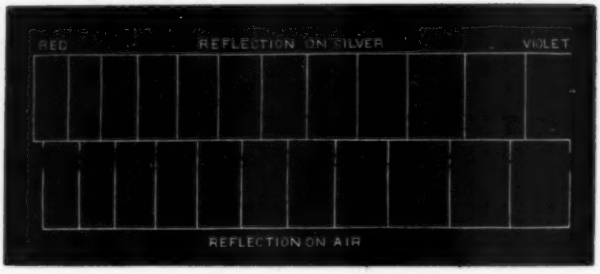
A very interesting paper has lately been published by O. Wiener (*Wied. Ann.*, **31**, 629, 1887) in which he attacks the problem of the determination of the thickness of the thinnest metallic plate which affects reflected light in the same way as a thick plate of the same metal.

It is well known that in general when light passes from a less dense to a more dense transparent medium, the phase of the reflected ray is altered by half a wave-length. This is proved by the fact that the centre of Newton's rings as seen by reflected light is black. For the difference in the phases of the rays reflected from the front and back surfaces of the film respectively depends partly on the thickness of the film and partly on any change of phase which the rays may undergo on reflection or refraction. As the film becomes very thin the difference in the paths of the two rays due to its thickness

becomes negligible, and thus if the phase were not affected by reflection or refraction, the rays reflected from the centre of the rings where the film is thinnest would be nearly in accord, or the centre would be bright when viewed by reflected light. The fact that the centre is dark is explained by the assumption that when a ray of light passes from a less dense to a more dense transparent medium the phase of the reflected ray is altered by half a wave-length.

When light is reflected at a metallic surface, an alteration of phase also takes place, but it is not necessarily half a wave-length, and it is on this peculiarity that Wiener's method is based.

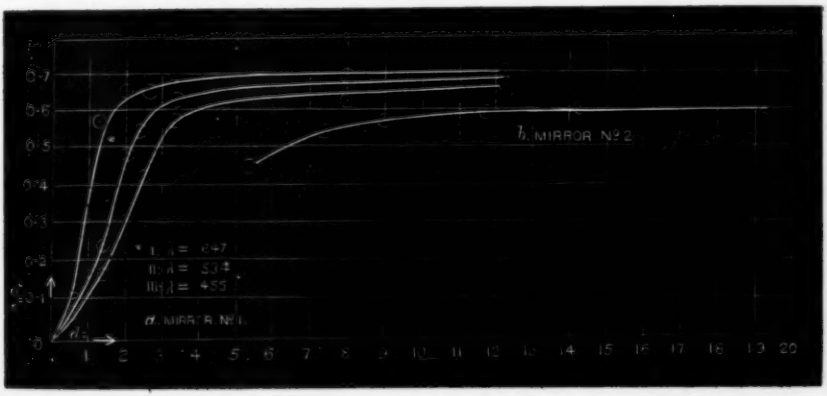
In the light reflected from a thin film of air enclosed between the two glass plates, those rays will be wanting for which the difference of phase produced (1) by the difference in the lengths of the paths of the rays reflected at the first and second surfaces, and (2) by the change of half a wave-length produced on reflection at the air-glass surface, is an odd multiple of half a wave-length. In the spectrum of such light, dark interference bands will be visible corresponding to the missing rays. If the second surface had been silvered (the thickness of the air film remaining unaltered) the effect of the first of the above two causes would be the same as before, but that of the second would be different. Hence the particular kind of light for which



the total retardation was previously an odd multiple of the half wave-length would no longer satisfy that condition, and the interference bands in the spectrum would occupy new positions. If the second surface had been partly silvered, two contiguous spectra could be obtained in which the interference bands appeared broken.

In the experiments with which we are specially concerned, Wiener proceeded as follows:—A thin film of mica was partly covered by a second with a straight edge. Silver was deposited on it by discharge from a silver electrode (*Wied. Ann.*, **29**, 353, 1886). The layer thus formed was thickest in the centre, and thinned away gradually. When the covering mica was removed, the silver film was bounded on one side by a straight line. Thus when light was reflected from the

film on to the slit of a spectroscope (the silvered side being furthest from the instrument), two spectra were seen side by side, as is shown in the figure (p. 246). The displacement of the interference bands varied with the thickness of the film, but became constant when the thickness exceeded a certain value. It was measured for certain parts of the spectrum at a number of points, the positions of which on the mica were determined. The silver was then converted into silver iodide, and the displacement of the interference bands was again determined at the selected points. From this latter measurement, the thickness of the iodide, and therefore of the original silver film, could be deduced by formulæ, for the discussion of which I must refer to the original paper (*loc. cit.*, p. 664). Curves were then drawn, showing the relation between the thickness of the silver and the change of phase produced by it. These are reproduced in the figure. Curves I, II, and



III were obtained by the same mirror, but by observations in different parts of the spectrum. Curve I corresponds to the orange ($\lambda = 647$), II to the green ($\lambda = 534$), and III to the blue ($\lambda = 455$). The retardation increases very rapidly for the blue, less rapidly for the other colours, till a thickness of about 4 $\mu\mu$. is attained. Afterwards it alters more slowly, and is nearly constant at the greatest thickness for which the measurements were made, viz., 12 $\mu\mu$.

Observations made with another mirror confirmed the result that the change of phase reached its maximum value for a thickness of about 12 $\mu\mu$., but indicated a more uniform rate of increase. Herr Wiener ascribes this difference to a slight oxidation of the silver films.

The smallest thickness for which any displacement of the bands could be observed is estimated as rather less than 0·2 $\mu\mu$.

We have now reached the point at which we may investigate the inferior limit to the range of molecular forces, viz., the so-called

radius of the molecules. This part of my subject has been so fully discussed by Sir William Thomson (*Natural Philosophy*, Thomson and Tait, Pt. II, 495, 1883; *Proc. Roy. Instit.*, 1883; *Exner's Rep.*, **21**, 182, 1885) and O. Meyer (*Die Kinetische Theorie der Gase*, 225, 1877) that it will be unnecessary for me to reproduce their arguments in full. I shall therefore content myself with shortly stating their results, and describing at greater length a more recent method developed by Dorn and Exner.

Sir William Thomson (*Natural Philosophy*, 502) concludes that the diameter of the gaseous molecule cannot be less than 0·02 $\mu.\mu.$, and that the distance from centre to nearest centre in solids and liquids may be estimated at from 0·07 to 0·02 $\mu.\mu.$

He points out that when plates of zinc and copper which are connected by a metal approach each other, work is done in virtue of the attraction caused by their assuming different electrical potentials. If the plates are split up into an increasing number of thin layers and arranged Zn and Cu alternately, so that the thicknesses of the plates and of the intervening spaces are equal, the work done will vary as the square of the number of plates. If the thickness in question were 0·1 $\mu.\mu.$, the heat-equivalent of the work done would be sufficient to raise the temperature of the metals by 62° C., if it were 0·025 $\mu.\mu.$ the heat would suffice to raise the mass through 992° C. The conclusion is drawn that the molecules of Zn and Cu are probably at least 0·1 $\mu.\mu.$, and certainly more than 0·025 $\mu.\mu.$ in diameter. Again, when a liquid film is stretched, work is done upon it, and it is also cooled. To keep its temperature constant heat must be supplied, and if the thickness were reduced to 0·05 $\mu.\mu.$, the heat-equivalent of the total amount of energy imparted to the film would be about twice the latent heat of steam. As it is incredible that the film could absorb so large a quantity of energy and yet remain in the liquid state, it is certain that if it could be reduced to this extreme tenuity, the work done in stretching it would, *cæteris paribus*, be less when it was very thin than when it was relatively thick. Hence the surface tension must diminish before the thickness of the film is 0·05 $\mu.\mu.$, and Sir William Thomson thinks that there cannot "be any considerable falling off in the contractile force as long as there are several molecules in the thickness. It is therefore probable that there are not several molecules in a thickness of" 0·05 $\mu.\mu.$ From a consideration of the transmission of light through transparent bodies, he also concludes that the distance between the centres of contiguous molecules in solids and liquids is greater than 0·05 $\mu.\mu.$

The fourth method used by Sir William Thomson is based on the theory of gases. An important formula has been deduced by Clausius, and, in a slightly different form, by Maxwell, which establishes a

relation between the diameter of the molecule (d), the mean free path (L), and the ratio of the total volume of the molecules to the volume of the gas (v). It may be written

$$d = 6\sqrt{2}v\mathrm{L}.$$

The value of v, which is called by Loschmidt the condensation coefficient, has been obtained in various ways. Sir William Thomson concludes from the general results of experiments on the condensation of gases, that a gas could not be made 40,000 times denser than it is under ordinary atmospheric pressure and at ordinary temperatures. Hence $v > 25 \times 10^{-6}$.

Loschmidt (*Sitzungsber. Wien. Akad., math. Classe*, **52**, Abt. 2, 404, 1866) made use of Kopp's formula—specific volume = molecular weight divided by the density at the boiling point—to calculate the densities in the liquid state of gases which had not then been liquefied. He assigned to the various elements specific volumes somewhat different from those selected by Kopp. Thus assuming those of oxygen and nitrogen to be 11 and 12 respectively, the calculated densities are $16/11 = 1{\cdot}4545$, and $14/12 = 1{\cdot}1666$. Hence, taking air as a mixture of four parts of nitrogen and one of oxygen, he calculated the density in the liquid state to be 1·224. If the molecules are spheres, they will, when packed as closely as possible, occupy a space which bears to the sum of their volumes the ratio 1·17 : 1. He assumes that in a liquid they are closely packed, and deduces as an approximation to the true density $1{\cdot}224 \times 1{\cdot}17 = 1{\cdot}5$ say. Hence $v = 0{\cdot}001293/1{\cdot}5 = 0{\cdot}00086$. He takes as the value of the mean free path 140 $\mu\mu$., whence $d = 1$ $\mu\mu$. If, however, we use the value of L given by Meyer (*Die kinetische Theorie der Gase*, 140), viz., 95 $\mu\mu$., we get $d = 0{\cdot}68$ $\mu\mu$.

O. Meyer (*Theorie der Gase*, 225), employing a similar method for nine substances, the density of which is known both in the liquid and gaseous states by direct experiment, found values for the molecular diameters which lie between 1·18 $\mu\mu$. for N_2O and 0·44 $\mu\mu$. for H_2O.

Dorn (*Wied. Ann.*, **13**, 378, 1881), and more recently Exner (*Rep. der Physik*, **21**, 446, 1885) have obtained the value of the so-called condensation-coefficient, v, in another way.

Clausius (*Die mechanische Behandlung der Electricität*, III Abschnitt) has given a formula which connects K, the specific inductive capacity of a dielectric, and v as above defined, on the assumption that the molecules of the dielectric are conductors, and are surrounded by a non-conducting medium. This formula is—

$$v = \frac{\mathrm{K} - 1}{\mathrm{K} + 2}.$$

According to Maxwell's electromagnetic theory of light, if n is the

refractive index of the dielectric for rays of infinite wave-length $K = n^2$, at all events to a first approximation. This equation is not satisfactorily fulfilled in the case of liquids or easily condensible gases, partly, perhaps, because our knowledge of the law of dispersion is insufficient to enable us to calculate the value of n from the refractive indices of the comparatively short luminous and dark waves which have been studied experimentally. In the case of gases in which the dispersion is very small, this difficulty is not met with. As the specific inductive capacity is also very nearly unity, the experimental difficulties which attend its determination are great. The first measurements of this kind were made by Boltzmann and Professors Ayrton and Perry. More recent observations of Klemenčič are in good accord with the results obtained by Boltzmann. The agreement between the values of $\sqrt{K}$ and of n, as determined by Mascart, is not satisfactory for vapours, but is very close in the case of the more perfect gases. The following table is abstracted from that given by Klemenčič (*Exner's Rep.*, **21**, 611, 1885):—

	$\sqrt{K}$. Boltzmann.	$\sqrt{K}$. Klemenčič.	n.
Air	1·000295	1·000293	1·000293
H_2	1·000132	1·000132	1·000139
CO_2	1·000473	1·000492	1·000454
CO	1·000345	1·000347	1·000335
N_2O	1·000497	1·000579	1·000516

This table shows that the value of v may be approximately determined in the case of gases for which we know either K or n. As v is the ratio of the space occupied by the molecules to the total volume of the body, of which the former is a constant and the latter varies inversely as the density (δ) of the substance, it is evident that for each substance v/δ should be a constant. Hence $(n^2 - 1)/\delta(n^2 + 2)$ should be the same at all temperatures and for all physical states of the same substance.

This result has been obtained independently from optical considerations by H. A. Lorentz (*Wied. Ann.*, **9**, 641) and L. Lorentz (*Wied. Ann.* **11**, 70), and has been tested experimentally by the latter and Prytz (*Wied. Ann.*, **11**, 104) in a large number of cases. Although the refractive indices are those for D, and not for waves of infinite length, the agreement is very close.

I give in the following table, as samples, the first three substances mentioned in the final tables of these two observers. The numbers

compared are the values of $(n^2 - 1)/\delta(n^2 + 2)$ for the same substance in the liquid and gaseous states :—

Substance.	Observer.	Liquid.	Vapour.
Ethyl ether	L	0·30264	0·3068
Ethyl alcohol.....	„	0·28042	0·2825
Water	„	0·20615	0·2068
Methyl alcohol	P	0·2567	0·2559
Methyl acetate.....	„	0·2375	0·2399
Ethyl formate	„	0·2437	0·2419

The following table contains the values of v for some of the elements. From Avogadro's law, it follows that these numbers are proportional to the volumes of the molecules; and if we divide them by the number of atoms in the molecule we obtain numbers proportional to the atomic volumes. In the case of H_2, v was determined from the specific inductive capacity, in all other cases from the refractive index. In this and the next table, I quote from Exner.

Substance.	Molecular volume, 10^{-5} ×	Atomic volume, 10^{-5} ×
H_2.....	8·8	4·4
N_2.....	20	10
O_2.....	18	9
Cl_2.....	51	25
S_4.....	108	27
P_4.....	91	23
Hg	37	37
C (from CO − O)	—	14

From these atomic volumes it is of course possible to calculate the molecular volume of any compound of these substances. Thus the molecular volume of water = 8·8 + 9 = 18 nearly.

The following table gives the values of v obtained from K in the cases of the first five substances, and from n in that of the others, together with the calculated values deduced from the above atomic volumes :—

Substance.	v (observed), 10^{-5} ×	v (calculated), 10^{-5} ×
Air	17*[20]	19
CO_2	31	32
N_2O	33	34
CH_4	31	32
C_2H_4	44	45
NH_3	26	23
H_2O	17	18
NO	20	19
H_2S	43	36
HCl	30	29
C_2N_2	56	48
SO_2	44	45

These results, on the whole, confirm the accuracy of the physical meaning of the expression $(n^2 - 1)/(n^2 + 2)$, and tend to show that the diameter of the molecule is the same in the liquid and gaseous states. It is important to note, however, that from the theoretical point of view there is a good deal of confusion. The meaning of the expression $(K - 1)/(K + 2)$ is deduced from an electrical theory put forward by Clausius. It should only be equivalent to $(n^2 - 1)/(n^2 + 2)$ when n is calculated for waves of infinite length, and as a matter of fact K and n^2 are not equal for most vapours when n has a value proper to any of the visible rays. If then $(K - 1)/\delta(K + 2)$ is really the same for a liquid and its vapour, for neither of which n_∞ is known, we should not *primâ facie* expect that $(n^2_D - 1)/\delta(n^2_D + 2)$ would be the same for both. Nevertheless experiment shows that the variations produced in this expression by the passage from the liquid to the vaporous state are less than the discrepancies due to the imperfect agreement between the values of K and n^2 in the case of most vapours for which both have been determined. In cases where K is not $= n^2$, the value of v deduced from n^2 is to be preferred. Thus the specific inductive capacity of flint glass, as determined by Dr. Hopkinson (*Proc. Roy. Soc.*, **43**, 161), is 9·5, which makes v nearly $= 0{\cdot}8$. If we assume the refractive index to have been 1·7, we get v rather less than 0·3, which is in far better agreement with the results obtained from gases. In the case of conductors, the values of K are very high.

The annexed table gives the value of v for several liquids, calculated directly from K and n^2, as determined by Dr. Hopkinson (*loc. cit.*). The value is also given deduced from the atomic volumes of the gases,

* This number appears to be incorrect. Boltzmann's value for K is 1·000590, which gives $v = 20 \times 10^{-5}$. This will be used hereafter.

viz., 14×10^{-5} for C, and $4{\cdot}4 \times 10^{-5}$ for H. Thus for the substance the chemical formula of which is C_nH_m, we have—

$$v = \frac{(14n + 4{\cdot}4m)10^{-5}}{\frac{12n + m}{2} \times 0{\cdot}00008961} D,$$

where D is the density of the liquid.

Substance.	Formula.	K.	μ^2.	v(K).	$v(\mu^2)$.	v calculated.
Amylene..	C_5H_{10}	2·05	1·9044	0·260	0·232	0·237
Benzol ...	C_6H_6	2·38	2·2614	0·315	0·296	0·278
Toluol....	C_7H_8	2·42	2·2470	0·321	0·291	0·286
Xylol	C_8H_{10}	2·39	2·2238	0·317	0·290	0·284
Cymol....	$C_{10}H_{12}$	2·25	2·2254	0·294	0·290	0·295

In these cases, then, all three methods of calculating v indicate that from one-fourth to one-third of the volume of the liquid is filled with matter.

Another interesting point is that this method of regarding the formula $(n^2-1)/\delta(n^2 + 2)$ enables us to assign a physical meaning to the specific refraction of a substance.

In the above calculations, it has been assumed that the atomic volume of a substance is the same, whatever the nature of its union with the other atoms may be. Landolt, however (*Liebig's Annalen*, **213**, 1882, 75) has undertaken a careful comparison of specific refractions calculated by the ordinary formula $(n-1)/\delta$ and by $(n^2-1)/\delta(n^2 + 2)$. He finds that the latter is more constant when the values obtained for the liquid and gaseous states are compared, and he calculates the specific atomic refractions by means of it. He finds it necessary to assign different values to O′ and O″, which from the point of view we are discussing, indicates a difference of atomic volume. It must also be remarked that a very low value of the specific inductive capacity of air when the pressure was 0·001 mm. has been obtained by Professors Ayrton and Perry, which might, if confirmed by future experiment, affect the questions we have been discussing. The following table of their results is abridged from Ayrton's *Practical Electricity*, p. 310. The numbers which refer to air are alone extracted.

The letter k indicates that the specific inductive capacity of air at 760 mm. is taken as unity.

Approximate pressure in mm.	k.
0·001	0·994* (about)
5	0·9985
760	1·0000

They have in a pamphlet "On Certain Modifications that must be Introduced in the Fundamental Notions of the Mathematical Theory of Electricity," p. 5, proved that if δ be the density referred to air at 760° mm. and 0° C. as unity, if 1·000294 be the refractive index of air under the same standard condition referred to that of a vacuum as unity, and if k be defined as above—

$$k = \frac{0{\cdot}000588\delta + 1}{1{\cdot}000588}.$$

This expression is obtained by Biot and Arago's formula $(n^2-1)/\delta$ = constant, but a practically identical result will be attained if we use instead the expression employed by Exner. It follows that k has a limiting value when $\delta = 0$, such that if k_0 is the specific inductive capacity of a vacuum referred to that of air at 760 mm. as unity, $k_0 = 1/1{\cdot}000588 = 0{\cdot}999412$. At 5 mm. $k = 0{\cdot}999416$, as given by the formula. This agrees with the value obtained by Boltzmann, viz., 0·99941 (*Practical Electricity*, *loc. cit.*), but is not in such close agreement with that obtained by Ayrton and Perry themselves. The difference might easily be ascribed to errors of experiment, but the value 0·994, when the pressure was 0·001 mm., was obtained in a later research (*Rep. Brit. Ass.*, 1880.) Its accuracy is independent of that of the measurements at a pressure of 5 mm., and as far as I am aware, no other observers have carried out experiments in gases of such extreme tenuity.

It is therefore much to be desired that further observations should be made on the specific inductive capacity of air at low pressures. The importance of such a research would be enhanced from the fact that it has been pointed out by Professor Fitzgerald (*Rep. Brit. Ass.*, 1880, *loc. cit.*) that the values obtained for the capacity of an air condenser between "about 0·02 and 0·2 mm. pressure bear a general resemblance to those obtained for the Crookes' force." For my present purpose, however, it is sufficient to remark that if the ratio of the specific inductive capacities of air at pressures of 0·001 and 760 mm. is about 0·994 : 1, then either Maxwell's theory fails when

* This number is correct. Professor Ayrton informs me that that given in *Practical Electricity*, viz., 0·94, is a misprint.

applied to rare gases, or the refractive indices of air at these pressures are in the ratio $\sqrt{0{\cdot}994} : 1$ that is $0{\cdot}997 : 1$. Now the fact that the refractive index from a vacuum to air at atmospheric pressure is about $1{\cdot}000294$, is proved not only by direct experiments on air of different densities, but also by the agreement between the observed and calculated results of the effect of atmospheric refraction on the apparent positions of stars. Hence if we admit the validity both of the experimental determination of the specific inductive capacity of air at a pressure of 0·001 mm., and of the application of Maxwell's theory of this case, we must conclude that the refractive index of highly rarefied air referred to that of a vacuum as unity is $0{\cdot}997 \times 1{\cdot}000294 = 0{\cdot}997293$, and that it is about 0·27 per cent. less than that of a vacuum. The alteration in the ordinary refractive index of air which would be required to make this quantity >1, would make the calculated atmospheric refraction nearly ten times greater than that which is actually observed. It is therefore evident that either the experimental result is affected with error, or that Maxwell's theory does not apply to a rare gas. In either case, the conclusions arrived at need not affect the application of Maxwell's theory to substances for which $K = n^2$, and for which, therefore, it appears to be at all events an approximation to the truth.

The values of v obtained by Exner are remarkably confirmed by those deduced from the theory of Van der Waals. In the general relation between pressure, volume, and temperature given by him, a constant b occurs which is, according to Van der Waals, $= 4v$, and, according to O. Meyer, $= 4\sqrt{2}v$.

The value of b may be obtained in several ways. Meyer deduces it from a comparison between the terms of Van der Waals' formula and the constants of a similar empirical formula of Regnault's. The values so obtained are of the same order as those given by other methods, but I do not think that Meyer's plan is as satisfactory as those adopted by Van der Waals himself, as it largely depends on the value of a very small constant in the empirical formula.

Van der Waals makes two comparisons—the one with Regnault's observations (*Die Continuität*, &c., 73 to 79) and the other with Cailletet's results (*loc. cit.*, 98 and 99), and he shows that the constants obtained by the former method produce a fair agreement with the observations of Andrews (*loc. cit.*, 80).

The table is obtained by taking these results (comp. Meyer, *Kinetische Theorie*, 75) and reducing all values to the standard pressure of one atmosphere.

	Value of b from		Mean value of b.	Value of v according to	
	Regnault.	Cailletet.		Van der Waals, $b = 4v$.	O. Meyer, $b = 4\sqrt{2}v$.
Air	0·00195	—	0·00195	0·00049	0·00035
H_2	0·00049	0·00050	0·00050	0·00012	0·000088
CO_2	0·0023	—	0·0023	0·00057	0·00041

The value of b for SO_2 deduced from experiments by Cagniard de la Tour is 0·0032, which leads to $v = 0·0006$ according to Meyer's formula. As these early observations were probably not so accurate as the others we are discussing, I shall not make use of his results, also as Meyer's relation between b and v appears to be the best, I shall hereafter employ it only.

Before discussing this table further, I must point out that there are some slight errors in the books which deal with the subject, and which account for discrepancies between the figures as given by others and by myself. The numerical value of b, which is proportional to the ratio of the volume of the molecules to the volume of the gas under standard conditions, increases with the standard pressure, and may be taken as proportional to it.

The values obtained by Van der Waals from Regnault and Cailletet's results are referred to pressures of 1 m. and 760 mm. respectively. Ruhlmann (*Mechanische Warmetheorie*, **2**, 244, Vieweg und Sohn, 1885) reduces them all to a pressure of 1 metre, but in so doing he *multiplies* the numbers which are referred to an atmosphere by 0·76 instead of dividing. Thus, as corresponding to 0·00198, he gives 0·0015, and so on. By this mistake, he conceals the practical identity of the values obtained by Van der Waals.

O. Meyer himself makes a similar mistake. The value of b for CO_2 referred to a pressure of 1 m. is 0·003 (*Die Continuität*, &c., 74). Van der Waals calculates it for 1 atmosphere on p. 80, and finds $b = 0·0023$. Yet Meyer (*Kinetische Theorie*, 231) treats this value as though it referred to the larger pressure, and finds that for CO_2 $d = 0·18$ $\mu.\mu.$ instead of 0·23 $\mu.\mu.$, which is the correct value deduced from his other data. I point out these errors only to prevent confusion on the part of those who might happen to compare the different tables of values.

In the next table are the values of v obtained from the specific inductive capacity, the refractive index, and the theory of Van der Waals:—

Table of Values of v.

	Calculated from K, as determined by		Calculated from n, Mascart. 10^{-5} ×	Calculated from b, Van der Waals and O. Meyer, 10^{-5} ×
	Boltzmann, 10^{-5} ×	Klemenčič, 10^{-5} ×		
Air	20	20	20	35
H_2	8·8	8·8	9·3	8·8
CO_2	32	33	30	41

Without laying stress on the extraordinary similarity between the values of v obtained in the case of H_2 from the dynamical theory of gases, and from electrical and optical formulæ, I think that the agreement as to the order of the magnitudes of v calculated by such various methods is very strong evidence that they are approximately correct. It will also be observed that they are intermediate in value between the superior and inferior limits given by Loschmidt and Sir William Thomson respectively.

Loschmidt regarded the liquid as formed of molecules in contact, an assumption which could not give too small a value for v; Sir W. Thomson selects a condensation coefficient, which he is sure is not large enough. We thus get in the case of air—

Superior limit (Loschmidt)	86	× 10^{-5}
Actual value calculated from b	35	× 10^{-5}
,, ,, ,, n	20	× 10^{-5}
,, ,, ,, K	20	× 10^{-5}
Inferior limit (Sir W. Thomson)	2·5	× 10^{-5}

We may, therefore, conclude that the space occupied in the sense previously defined by the molecules in air at 0° C. and 760 mm. is about one five-thousandth (0·0002) of the volume of the gas. As Loschmidt's calculation is based on the assumption that in a liquid $v = 1/1·17 = 0·85$, and as Exner's value in the above table is 20/86 of his, it follows that in liquid air the value of v would be about 0·2. Very similar values are obtained for substances which can be liquefied easily. Thus the observed value of v for water vapour is 0·00017. This is referred to 0° C. and 760. But at 0° C. and 4·6 mm. (the maximum tension of aqueous vapour at that temperature), the volume of saturated steam is 210,660 times the volume of the liquid. Under standard conditions this would be reduced to 210,660 × 4·6/760 = 1275.

Hence for liquid water $v = 0{\cdot}00017 \times 1275 = 0{\cdot}22$. We conclude that in liquids about one-fifth only of the total volume is filled with matter, which is in fair accord with the numbers before obtained from Hopkinson's results.

To calculate the diameter of a molecule we must know not only v but also L. This may also be determined by three independent methods of experiment, viz., by the determination of the coefficients of viscosity, diffusion, and thermal conductivity. As the values of the coefficient of viscosity given by Meyer are not reduced to 0° C., I take the values of L deduced from these given by Ruhlmann (*Mechanische Warmetheorie*, 227). For those which depend on diffusion, I quote Stefan's deductions from Loschmidt's experiments as given by Exner (*loc. cit.*, 450). Taking the coefficients of thermal conductivity determined by experiment by Kundt and Warburg, Winklemann and Stefan, as given by O. Meyer (*loc. cit.*, 194), I have calculated back to the coefficients of viscosity by the formula $\xi = 1{\cdot}53\eta c$, where ξ and η are the coefficients of conductivity and viscosity, and c is the specific heat at constant volume, and have then deduced L from the coefficient of viscosity thus calculated. The results are given in the following table, and prove that there is at all events no doubt as to the order of the magnitude of L.

Values of L.

Substance.	L in $\mu\mu$. calculated from		
	Viscosity.	Diffusion.	Thermal conductivity.
Air.....	99	71	110
H_2.....	194	139	186
CO_2.....	66	50	55
CO	97	65	106
N_2O	66	42	59

We are now, if the various theoretical assumptions are allowed, in a position to calculate the diameter of a molecule of air, H_2, or CO_2, by three absolutely independent methods. We may combine the values of v obtained from the specific inductive capacity, the refractive index, and the theory of Van der Waals, with the values of L deduced from the coefficients of viscosity, diffusion, and thermal conductivity respectively. The results are shown in the following table :—

Substance.	Diameter of gaseous molecule in $\mu.\mu.$ calculated from		
	Specific inductive capacity and viscosity.	Refractive index and diffusion.	Expansion and thermal conductivity.
Air.....	0·17	0·12	0·33
H_2.....	0·14	0·11	0·14
CO_2.....	0·18	0·13	0·19

Without insisting too much on an agreement which can be exemplified in the case of a few gases only, and which would probably not be exhibited by the results of experiments on vapours, it is not too much to say that it cannot possibly be fortuitous, and that it leaves very little doubt that the so-called diameter of a gaseous molecule is of the same order of magnitude as 0·2 $\mu.\mu.$

In conclusion, I think it may be well to attempt to class the phenomena which have been observed in very thin layers of matter, and the results of calculations on the size of molecules, in the order of the magnitudes involved. It is probable that such a statement will have to undergo much correction in the future, but it may be useful and suggestive in the present. At all events, I think it will show that the time has passed when any estimate, however rough, as to the magnitude of molecules or of the radius of molecular action is to be welcomed. We know now what the order of these magnitudes is, and observations are wanted, based on reliable methods, and leading to definite results.

In drawing up such a table I shall, therefore, reject measurements which appear to me to be open to very grave doubt.

In the first place, all results as to the condensation of liquid films on solids which lead to values of the radius of molecular action of several hundred or even several thousand micromillimetres must be rejected until they are confirmed by other methods. The *onus* of proving that the bodies used are not porous, not absorbent, and not affected with impurities which can unite chemically with, or dissolve in, water, lies with the investigators who adopt this method. Not only have the observations on agate, varnished metals, and glass, shown that these are grave and probable sources of error, but Ihmori has proved that when they are as far as possible got rid of the thickness of the condensed film is very small. The fact that soap films exhibit no trace of change in their surface-tension or other properties till a thickness of about 50 $\mu.\mu.$ is reached, makes it absolutely incredible that the radius of molecular attraction should have a magnitude of

from 500 to 3000 $\mu.\mu.$ In this view I am supported by the opinion of Sir W. Thomson, who has laid it down as "quite certain that the molecular attraction does not become sensible until the distance is much less than 250 micromillimetres" (*Proc. Roy. Inst.*, **11**, Part III, 415, 1887).

Important, too, as the observations of Ihmori and Warburg are, I do not think that they can be used for our present purpose. They refer only to the temporary film, and therefore do not afford direct information as to the distance between the surface of the glass and the outermost water layer. This is given by Bunsen's observations, though it is doubtful what the nature of the attraction by which the water is held may be.

I shall also reject calculations based on the polarisation produced by gases. The uncertainty as to the density of the films deprives these estimates of all value. The same objection does not, however, apply to measurements of the thickness of the electrical double layer. I shall therefore include these and the results of observations on the polarisation of metal by metal, subject of course to the criticisms which I have already made. I include Plateau's results on account of their historical interest.

Table of Properties of Thin Films and of Molecular Magnitudes.

118 $\mu.\mu.$

Superior limit to the radius of molecular action, deduced from Plateau's experiments on the pressure of a soap bubble by Maxwell's theory that the surface-tension first diminishes when the thickness of the film $= \rho$.

96—45 $\mu.\mu.$

Between these limits, the thickness of a film begins to be unstable, that is, the surface-tension begins to diminish. Hence the radius of molecular action must be < 96 $\mu.\mu.$, and > 22 $\mu.\mu.$

59 $\mu.\mu.$

Superior limit to ρ deduced by Plateau on the assumption that the surface-tension first diminishes when the thickness $= 2\rho$.

50 $\mu.\mu.$

Value of ρ deduced by Quincke from experiments on capillary elevation. Hence the thickness should begin to be unstable when it is 100 $\mu.\mu.$ or 50 $\mu.\mu.$, according as we adopt Plateau's or Maxwell's views. Probably the truth lies between the two. There is therefore a remarkable accord between Quincke's result and the superior limit

to the unstable thickness (96—45) obtained by Reinold and Rücker from experiment.

12 $\mu.\mu.$

Average thickness of black soap-films measured by two independent methods. As the tension of a black film is equal to that of a thick film, the surface-tension, which begins to diminish at 50 $\mu.\mu.$, must increase again and reach its original value at 12 $\mu.\mu.$ The fact that each black film is of uniform thickness proves that the surface-tension is still increasing at 12 $\mu.\mu.$, which is the lower limit to the range of unstable thickness. This is also about the thickness below which, according to O. Wiener, a thin silver plate will no longer produce the same effect on the phase of reflected light as a thick silver plate would do.

10·5 $\mu.\mu.$

Thickness of the permanent water film observed by Bunsen on unwashed glass at a temperature (23° C.) at which the vapour pressure of water is small.

4 $\mu.\mu.$ to 3 $\mu.\mu.$

Average distance from centre to nearest centre of molecules in gases under standard conditions calculated by Meyer. If Exner's values of v be accepted, the distance would be more nearly 2 $\mu.\mu.$

3 $\mu.\mu.$ to 1 $\mu.\mu.$

Thickness of metal films required to polarise platinum completely according to Oberbeck.

1 $\mu.\mu.$ to 0·02 $\mu.\mu.$

Thickness of electric double layer according to Oberbeck and Falck. Lippmann found 0·3 $\mu.\mu.$

0·2 $\mu.\mu.$

Smallest thickness of silver which affects the phase of reflected light.

0·14 to 0·11 $\mu.\mu.$

Diameter of gaseous hydrogen molecule as given by combining—
(1.) The specific inductive capacity and coefficient of viscosity.
(2.) The refractive index and coefficient of diffusion.
(3.) The law of expansion and the thermal conductivity.

0·07 to 0·02 $\mu.\mu.$

Average distance between centres of molecules supposed arranged

uniformly in liquids and solids according to Thomson. A superior limit found by L. Lorenz was 0·1 $\mu.\mu.$

0·02 $\mu.\mu.$

Inferior limit to the diameter of a gaseous molecule according to Thomson.

These results may be shortly summed up as follows:—

$\mu.\mu.$		
118	Superior limit to ρ	Plateau. (Maxwell).
96—45	Range of unstable thickness begins	Reinold and Rücker.
59	Superior limit to ρ	Plateau.
50	Magnitude of ρ	Quincke.
12	Range of unstable thickness ends	Reinold and Rücker.
12	Action of silver plate on phase of reflected light alters	Wiener.
10·5	Thickness of permanent water film on glass at 23° C.	Bunsen.
4—3	Mean distance between centres of nearest molecules in gases at 760 mm. and 0° C.	O. Meyer.
3—1	Thickness of metal films which polarise platinum	Oberbeck.
1—0·02	Thickness of electric double layer	Lippmann and Oberbeck.
0·2	Smallest appreciable thickness of silver film	Wiener.
0·14—0·11	Diameter of gaseous hydrogen molecule	Exner. O. Meyer. Van der Waals.
0·07—0·02	Mean distance between centres of nearest liquid molecules	W. Thomson.
0·02	Inferior limit to diameter of gaseous molecule	W. Thomson.

XXIII.—*On the Supposed Identity of Rutin and Quercitrin.*

By Edward Schunck, Ph.D., F.R.S.

Rutin, a crystalline yellow colouring matter, was discovered by Weiss (*Pharm. Centr.*, 1842, 903), who obtained it by treating the leaves of *Ruta graveoleus* with alcohol or acetic acid, and described some of its properties. It was next examined by Bornträger (*Annalen*, **53**, 385), who confirmed the statements of his predecessor, and also analysed the substance and its lead compound. Rochleder and Hlasiwetz (*Annalen*, **82**, 197) obtained from the capers of commerce, the flower-buds of *Capparis spinosa*, a colouring

matter having the properties of rutin, and the same composition as that given by Bornträger, and in 1858 (*Manchester Memoirs*, 2 Ser., **15**, 122) I showed that the same substance could be easily procured from the leaves of common buckwheat, *Polygonum Fagopyrum*. In a second investigation undertaken by himself, Hlasiwetz (*Annalen*, **96**, 123) found that, by the action of strong acids, rutin is decomposed, yielding quercetin and sugar, and the quantities of the two latter formed by its decomposition being very nearly those required in accordance with the then accepted formula of quercitrin, he concluded that quercitrin and rutin were identical. This conclusion seems to have been generally adopted by compilers of handbooks and dictionaries.

A few years later, however, Zwenger and Dronke (*Annalen*, **123**, 145) endeavoured again to prove that the two bodies were really distinct, and that though they were very similar in many respects they differed with regard to some of their properties, as well as in composition. The conclusion they arrived at was that whereas quercitrin was a compound of 1 mol. of quercetin with 1 mol. of sugar (dextrose ?) minus water, rutin contained 1 mol. of quercetin and 2 mols. of another kind of sugar. This conclusion is an approximation to what I believe to be the truth. If, however, it had been known at the time that the sugar formed by the decomposition of quercetin is isodulcite, $C_6H_{14}O_6$, and not glucose, and that rutin yields the same kind of sugar as quercitrin, the subject would have again been involved in the obscurity which the authors had attempted to remove.

Among the earlier memoirs on the subject, there is one by Stein (*J. pr. Chem.*, **58**, 399; **85**, 351; **88**, 280), who obtained from so-called Chinese yellow berries, the unexpanded flower-buds of *Sophora japonica*, a colouring matter which he considered to be identical with rutin from rue. Foerster (*Ber.*, **15**, 214), however, who has recently examined this substance, supposes it to be distinct, and has accordingly named it *sophorin*.

The properties of quercitrin and of its products of decomposition having of late years been minutely studied, and its composition accurately ascertained by Liebermann and Hamburger and others, and rutin, so far as I know, not having been anew examined, it seemed to me that it might be interesting again to compare the two substances, and if they were found to be distinct, to ascertain wherein the difference consists.

The quercitrin which I used was prepared in the usual way from quercitron bark. The rutin was obtained from *Polygonum fagopyrum* leaves, and though it had been kept for many years had undergone no change, and seemed quite pure.

The yellow colouring matter from buckwheat leaves has the same

properties as the rutin from garden rue, but the latter contains some impurity which is not easily removed, a fact already pointed out by Zwenger and Dronke. Rutin, even after numerous crystallisations, retains a faint greenish tinge, and may be described as being of a pale primrose-yellow, whereas the colour of quercitrin inclines more to lemon-yellow.

In the following table, the reactions in which the two substances show a marked difference are placed side by side; the reactions in which no difference could be observed are omitted.

Quercetin.	*Rutin.*
Soluble in 280 parts of boiling water.	Soluble in 170 parts of boiling water.
Soluble in 3·5 parts of boiling absolute alcohol.	Soluble in 5 parts of boiling absolute alcohol.
Soluble in 125 parts of ordinary ether.	Soluble in 335 parts of ordinary ether.
Easily decomposed when its watery solution to which sulphuric acid has been added is boiled.	Very slowly decomposed by the action of boiling dilute sulphuric acid.
When a dilute alcoholic solution containing silver nitrate is shaken up with three times its volume of ether, the latter acquires a crimson colour; the colour soon fades, metallic silver being at the same time deposited.	A dilute alcoholic solution containing silver nitrate shaken up with ether imparts to the latter a light yellow colour.
An aqueous solution gives with stannous chloride a light red precipitate.	An aqueous solution gives with stannous chloride a bright yellow precipitate.
By the action of bromine, crystallised tetrabromoquercitrin is formed.	By the action of bromine only amorphous products are obtained.
By the action of chlorine on the substance suspended in water a yellow body is formed which contains chlorine, and is insoluble in water, but soluble in alcohol, the alcoholic solution leaving,	On passing chlorine through water with rutin in suspension, the latter dissolves entirely. The solution, on evaporation over sulphuric acid, leaves a brown amorphous residue which has an

Quercitrin.	*Rutin.*
on evaporation, an amorphous residue.	astringent taste and shows some of the reactions of tannin, the watery solution giving a dark-green coloration with ferric chloride and a flocculent precipitate with gelatin.

Rutin dyes the same colours on mordanted calico as quercitrin, the alumina mordant acquiring a yellow and the iron mordant a more or less intense olive colour, but using equal weights of both substances the shades produced by quercitrin are perceptibly darker.

Rutin yielded on analysis the following results:—0·4686 gram of substance dried in the desiccator lost, on heating at 130°, 0·0186 gram water, equal to 3·97 per cent.

1·7352 grams substance dried in the desiccator lost, on heating at 130°, 0·0696 gram water, equal to 4·01 per cent.

I. 0·5510 gram substance dried at 130° gave 1·0588 gram CO_2 and 0·2623 gram H_2O.

II. 0·4748 gram substance dried at 130° gave 0·9152 gram CO_2 and 0·2348 gram H_2O.

These numbers correspond in 100 parts to—

	I.	II.
C	52·40	52·55
H	5·28	5·49

On adding sulphuric acid to a watery solution of rutin and boiling, yellow crystalline needles are deposited, consisting of a product of decomposition. The boiling must be continued for some time, the decomposition being much more slowly effected than with quercitrin. After cooling, the yellow needles are collected and washed. They have the properties of quercetin and also the same composition, as the following results of their analysis show:—

I. 0·5002 gram substance heated for 24 hours at 130° gave 1·0896 gram CO_2 and 0·1784 gram H_2O.

II. 0·2667 gram substance dried at 130° gave 0·5928 gram CO_2 and 0·0851 gram H_2O.

0·3050 gram quercetin from quercitrin gave 0·6700 gram CO_2 and 0·1022 gram H_2O.

These numbers correspond in 100 parts to—

	I.	II.	Mean.	Quercetin from quercitrin.
C	59·49	60·62	60·05	59·90
H.....	3·96	3·54	3·75	3·74

The formula $C_{21}H_{16}O_{11}$ for quercetin requires—

C.....	60·00
H.....	3·33

By acting on the product from rutin with acetic anhydride and sodium acetate, an acetyl compound was obtained crystallising in white needles and having the same appearance and showing the same melting point as the compound formed in the same way by acting on the quercetin from quercitrin.

The product soluble in water formed along with quercetin by the action of sulphuric acid on rutin is isodulcite. It is obtained from the filtrate, after removal of the acid, by evaporating to a syrup, dissolving the latter in absolute alcohol, adding several times its volume of ether to the alcoholic solution, and allowing the liquid after the milkiness caused by the addition of ether has subsided as a syrupy deposit, to evaporate slowly. The substance thus obtained has the same crystalline form and general properties as the isodulcite from quercitrin. Its melting point is 90—91°.

The products of decomposition of quercitrin and rutin with acids being the same, there remains only one way of explaining the difference between the two substances, and that is to suppose that the relative quantities of the products of decomposition formed differ in the two cases. Now the formula $C_{42}H_{50}O_{25}$, which I would propose for rutin, requires in 100 parts—

C.....	52·83
H.....	5·24

with which, as will be seen, the numbers found by experiment agree. According to Zwenger and Dronke, rutin dried at 150—160° contains—

C.....	52·66
H.....	5·00

numbers which also correspond with those required by the above formula.

The substance dried at 100° still retains, it would appear, 2 mols. H_2O, which are expelled at 130°. According to the formula $C_{42}H_{50}O_{25} + 2H_2O$, the loss on heating would be 3·63 per cent. Experiment, as stated above, gave 3·97—4·01 per cent.

The formula $C_{42}H_{50}O_{25} + 2H_2O$ requires—

C.....	50·90
H.....	5·45

The following numbers show the results obtained by various experimenters in the analysis of rutin dried at the ordinary temperature or at 100°:—

	Bornträger, from rue.	Rochleder and Hlaswietz, from capers.	Zwenger and Dronke, from capers.	Schunck, from buckwheat.
C	50·30	50·15	49·44	49·85
H	5·60	5·70	5·52	5·88*

If the formula given above be adopted, then the decomposition of rutin by acids must be represented by the following equation:—

$$C_{42}H_{50}O_{25} + 4H_2O = \underset{\text{Quercetin.}}{C_{24}H_{16}O_{11}} + \underset{\text{Isodulcite.}}{3C_6H_{14}O_6}.$$

In accordance with this equation, 100 parts of rutin should yield—

50·31 quercetin and
57·22 isodulcite.

Experiment gave—

48·50 quercetin and
55·20 isodulcite;

numbers which approximate to those required by theory and differ widely from the respective amounts, 60·76 and 46·08, corresponding with the formula $C_{36}H_{38}O_{20}$, which according to Liebermann and Hamburger is that of quercitrin.

It would appear therefore that whereas quercitrin contains 2 mols. of isodulcite to 1 of quercetin, rutin has 3 mols. of isodulcite to 1 of quercetin. This being admitted, the great resemblance subsisting between the two substances as well as the differences observed, such as in the degree of solubility and tinctorial power, would be easily explained.

I have been assisted in these experiments by Mr. Percy Carter Bell, whose services as a skilful manipulator and a careful worker I have much pleasure in acknowledging.

* These numbers agree still better with the formula $C_{42}H_{50}O_{25} + 3H_2O$, which requires in 100 parts—

C..... 50·00
H ..... 5·55

In accordance with this formula, the loss on heating should be 5·35 per cent. Zwenger and Dronke found that rutin dried at 100° lost on being heated for some time at 150—160°, 5·92 per cent. of water.

XXIV.—*On the Composition of Japanese Bird-lime.*

By Edward Divers, M.D., F.R.S., and Michitada Kawakita, M.E., F.C.S., of the Imperial University, Tōkyō, Japan.

No results worthy of publication seem to have been obtained in the examination of bird-lime until the year 1884, when J. Personne (*Compt. rend.*, **98**, 1585), made known those obtained by his father and himself. When that paper appeared, we ourselves had been for some time occupied with the investigation of Japanese bird-lime, and had already obtained results which proved to be in general agreement with those of Personne, and yet sufficiently unlike them, and, in some respects, in advance of them, to lead us to continue our work, although he had promised further attention to the subject. Up to the present date, however, nothing more from him has appeared, and we now offer this paper as an extension and partial confirmation of his observations.

Bird-lime, or *tori-mochi*, is prepared in Japan, just as it is in Northern Europe, from a species of holly, by macerating and pounding its inner bark in water, and afterwards picking out the fragments of crushed tissue from the viscid mass. Bird-lime exists ready formed in the bark in great abundance, and is not apparently modified in any way by fermentative action during its preparation. In Europe it is prepared from the common or prickly-leaved holly (*Ilex aquifolium*), but in Japan it is obtained from *Mochi-no-ki*, the *I. integra* of Thunberg (*Prinus integra*, H. and A.). We are not familiar with bird-lime as prepared in Europe, but judging from descriptions, Japanese bird-lime is like it, except perhaps in not having a greenish hue, although of that even we are not certain, since the Japanese product may well have it sometimes when quite freshly prepared. Bird-lime is extensively used in Japan, as in Europe, for catching birds and insects, and with the usually attendant cruelty.

In manuals of economic botany, we find enumerated as peculiar constituents of the holly, a bitter principle named *ilicine*, an aromatic resin, and bird-lime itself. In the account of bird-lime given in Ure's *Dictionary*, the true substance is not well distinguished from the viscid matter of mistletoe (*Viscum album*), examined by Reinsch, from which it appears to be entirely different.

Some Properties of Japanese Bird-lime.

The bird-lime is pale-greyish, nearly opaque, of faint, peculiar odour, almost tasteless, soft, elastic, tenacious, and adhesive to dry

surfaces, and slightly lighter than water. It can be preserved in water for an indefinite time without change, except on its upper surface. Exposed to air, it very slowly turns brown outside, and becomes coated with a thin brittle skin. If heated moderately, it gives off water, and above 100° froths from disengagement of steam. By the loss of its moisture, it becomes transparent, brown, and while hot of the consistency of cold oil. If now allowed to cool, it remains transparent, and forms a soft, solid mass, elastic, tenacious, and sticky as before, somewhat resembling Canada balsam in appearance. Ether, carbon bisulphide, chloroform, light petroleum, and benzene dissolve bird-lime, leaving a residue which although of not inconsiderable volume, is of little weight. Cold alcohol scarcely dissolves it at all, and even hot alcohol, which has some solvent action at first, attacks merely the surface-portion of the mass. The alcoholic solution as it cools deposits a nearly colourless, transparent, adhesive matter, differing but little from the purified bird-lime itself. Ether is much to be preferred to other solvents, because it yields a clear solution, whereas carbon bisulphide and the rest give milky liquids, owing to the presence of water. The ether solution mixed with alcohol becomes turbid and deposits a tenacious mass. Freed from water and particles of woody fibre, bird-lime undergoes scarcely any change when heated up to temperatures below 350°, merely becoming slightly fluorescent, and a little darker in colour, and acquiring a feeble, waxy odour. About the melting point of zinc, however, it undergoes destructive distillation, in which most of it comes over as fatty acids and fluorescent hydrocarbons of waxy and mild empyreumatic odour and buttery consistence; very little permanent gas is formed, and only a small carbonaceous residue is left. Bird-lime burns in the air with a bright, smoky flame.

It is not very sensitive to reagents. *Sulphuric acid* dissolves it slowly, forming a red liquid, which blackens only when heated, and which, when poured into water, gives a viscid precipitate, like bird-lime, but dark-coloured. Boiling *nitric acid* slowly dissolves it with partial oxidation, this solution also yields a precipitate with water. The sulphuric acid solution poured into concentrated nitric acid, and then diluted with water, yields a precipitate of a mixture of feebly nitrated compounds. Aqueous solutions of *potassium hydroxide* only slowly and slightly emulsify bird-lime; fusion with the hydroxide is attended with much darkening in colour, and leaves a mass which emulsifies in water. Potassium hydroxide in strong spirit slowly dissolves the greater part of purified bird-lime, producing a dark-coloured solution. In this way,—that is by continued boiling with strong alcoholic potash—bird-lime has been attacked by both Personne and ourselves, in order to determine its composition.

The Constituents of Bird-lime.

Personne has found bird-lime, prepared from *I. aquifolium*, to contain *water* 27, and *vegetable débris and calcareous salts*, 23 parts per cent., the remaining and essential part being some *caoutchouc*, *the compound ether or ethers of a new alcohol*, and other matters undetermined. The acids, or acid, forming the ethers were also not investigated by him. He isolated the caoutchouc by saponifying the ethers with alcoholic potash, which left the caoutchouc undissolved.

Japanese bird-lime is much cleaner than that described by Personne, containing only 2 per cent. of dry-bark fragments, and no separate lime salts. Its water content, however, is larger (probably because it is kept in stock under water), the percentage lost at 110—120° being 38. Caoutchouc forms about 6 per cent., leaving 54 per cent. as the proportion of compound ethers and allied matters.

The Bark, &c.—Of the 23 parts per cent. found in French bird-lime by Personne, some 13 parts consisted of *calcium oxalate.** On boiling out the bark fragments from Japanese bird-lime with sodium carbonate, some oxalate was dissolved out, but only in small quantity. The bark burnt to ashes gave as much as 6·3 per cent. of ash, principally calcareous and largely phosphate, but of course with some carbonate; but as the whole ash was only one-eighth per cent. of the entire bird-lime, and as only a little of the calcium salts was oxalate, Japanese differs in this respect remarkably from French bird-lime.

The Caoutchouc.—As we have stated, the caoutchouc can be separated by boiling out the purified bird-lime with alcoholic potash, and this is the best way of proceeding. It is, however, difficult to get it quite free from potash, and to this end needs to be repeatedly dissolved in ether, and reprecipitated by alcohol. The caoutchouc can also be separated by dissolving the bird-lime in ether, and precipitating the solution with 95 per cent. spirit, but then only very imperfectly, because the main constituent of the bird-lime is also precipitated in part. The caoutchouc of bird-lime is pale-yellow and transparent, highly elastic, and when heated evolves the well-known penetrating odour. A combustion gave carbon 86·56 and hydrogen 11·31 per cent., so that oxygen to the extent of 2 per cent. was present. Before weighing it out, it had been kept for some time at 120—130°. It left a trace of ash when burnt.

Other and Principal Constituents of Bird-lime.—We have not fully isolated these by proximate analytical methods, but their general

* Not *phosphate*, as stated in the abstract of Personne's paper in this Journal (46, 1365).

properties appear to be those of the partially purified bird-lime; for when a boiling alcoholic solution of bird-lime is evaporated and cooled, or, again, when an ethereal solution of bird-lime is mixed with a little alcohol to separate the caoutchouc, and then evaporated, in either case the solid matter obtained is like the partially purified bird-lime, except in being colourless when deposited from the alcoholic solution.

Products of the Saponification of Bird-lime, and their Isolation.—Saponification with alcoholic potash yields besides the residual caoutchouc, firstly, the potassium salt of *palmitic acid*, and a very little of that of a *semi-solid acid* which we have been unable to purify or identify; secondly, *two crystalline alcohols;* and thirdly, a small quantity of a *resinoïd substance.* The separation of these may be carried out in somewhat different ways, and is unavoidably tedious. The purified bird-lime is boiled for two hours with potash and 95 per cent. spirit, in a flask fitted with a reflux condenser; and the alkaline solution, decanted from the caoutchouc, is poured into dilute spirit, by which a voluminous, gelatinous precipitate is produced, consisting of the alcohols, with some of the resinoïd body and potassium palmitate. The precipitate is well broken up by stirring, collected on a cloth filter, pressed, and washed with dilute spirit.

Three ways of proceeding from this point have been employed by us. In one, the precipitate is diffused through dilute spirit, stirred well and warmed with calcium chloride solution. The now much less voluminous precipitate is repeatedly washed with water, dried, and extracted with ether, which leaves the calcium palmitate undissolved. Spirit of 95 per cent. may be used in place of ether, but as it dissolves out a little calcium salt, its use is less satisfactory. On evaporating the ether (or spirit), the alcohols and resinoïd body are obtained. A second way of proceeding is to warm the precipitate with water and hydrochloric acid until it has shrunken to a small volume, wash repeatedly with water, press moderately, and extract with light petroleum, which dissolves out the palmitic acid and some of the resinoïd substance, and leaves behind all the alcohols and the rest of the resinoïd substance. After treatment by either method, the resinoïd compound is separated by repeated extractions with warm 80 per cent. spirit. A small quantity of the alcohols at the same time dissolves, and may be partly recovered by precipitation with a very little water, and extracting the precipitate with 80 per cent. spirit. The third way of proceeding, which is simpler in execution than the others, but much less effective, is to use 70—80 per cent. spirit in place of the light petroleum in the second way of working. This dissolves out the resinoïd substance, as well as palmitic acid.

Personne's method of procedure is to pour the product of saponifi-

cation into water, to wash the precipitate with much water, treat it with acetic acid to neutral reaction, again wash, dry, dissolve in hot 90 per cent. spirit, cool, and crystallise out the bird-lime alcohol from the solution. We have not found this method to work well, on account of the great difficulty in washing properly the voluminous gelatinous precipitate, and in just neutralising it with acetic acid. This precipitate contains, besides the alcohols and resinoïd substance, much acid potassium palmitate, to which indeed its bulky nature is partly due, and we have found it far preferable to convert the potassium palmitate either into the calcium salt or into free acid, as above described. Personne seems not to have recognised the presence of any fatty salt in the precipitate containing the alcohols.

Separation of the Alcohols from each other, and their Purification.—The crude solid alcohols can only be fully separated from each other by fractional extraction with strong spirit, repeated until the products obtained are of constant melting point. The alcohols, already treated as described with 80 per cent. spirit to remove the resinoïd substance, are warmed with successive portions of spirit, increasing in strength from about 85 per cent. to over 90 per cent., each portion of the solvent depositing crystals of the alcohols as it cools, and each mother-liquor by successive evaporations yielding a series of other crystalline deposits, all similar in appearance. When the last mother-liquors are too small in quantity and too impure to yield a satisfactory product by further evaporation, they are rejected or worked up for the little resinoïd substance they contain. The portions of the alcohols least soluble in spirit consist principally of the one alcohol, and those most soluble of the other alcohol. By a repetition of the treatment with spirit, the intermediate portions yield other series of deposits of higher and lower degrees of solubility, the extremes of which contain the two alcohols. The portions of the less soluble alcohol are submitted to further fractionation until the part undissolved by hot 90 per cent. spirit, and that dissolved and deposited by it on cooling have the same melting point. It is then finally dissolved in hot 95 per cent. spirit, crystallised out and again tested as to its melting point. The most soluble crystalline deposit, consisting principally of the more soluble alcohol, requires much further fractionation, in order to separate the less soluble alcohol on the one side, and the resinoïd substance on the other, so that the ultimate yield of the pure alcohol becomes very small. In fractionating out this alcohol, spirit of 85 per cent. is used, but finally this alcohol, like the other, should be crystallised out from 95 per cent. spirit, in order to get good crystals.

Personne observed the comparative insolubility of the solid alcohol in 80 per cent. spirit, but making no use of this fact, he purified the cake of crude solid alcohol by repeated crystallisations from boiling

90 per cent. spirit. During the purification, he met with a substance of peculiar form, visible under the microscope, and less soluble in spirit than the solid alcohol, and this he found to be gradually removed by repeated crystallisation. We have met with no such substance in Japanese bird-lime.

Purification of the Resinoïd Compound.—This is found mainly in the 80 per cent. spirit used to wash the crude alcohols after they have been separated from palmitic acid. When this separation has been effected in the second way, the spirit contains some fatty acids also. The light petroleum used to dissolve out palmitic acid also contains some of the resinoïd substance. In order, therefore, to separate palmitic acid, the residue, after evaporating the petroleum spirit, is dissolved in alcoholic potash, the palmitic acid precipitated by calcium chloride, water added, and the precipitate washed, dried, and extracted with ether. On evaporating the ether, the resinoïd substance is left, still mixed with some of the alcohols, but free from any fatty acid. The impure product is dissolved in strong spirit, and left to evaporate slowly. The alcohols separate as indistinctly crystalline, opaque matter, while the resin separates on the bottom and sides of the vessel as a translucent, gummy deposit, still containing spirit; the resin is then redissolved in spirit and the solution left to evaporate for two hours. On repeating these operations several times, it is obtained in a condition in which it has no longer any tendency to deposit crystalline matter.

Separation and Purification of the Fatty Acids.—By far the greater part of the fatty salts remain dissolved when the saponified bird-lime solution is poured into dilute spirit. The filtrate and washings from the gelatinous precipitate of alcohols are diluted with water, mixed with hydrochloric acid, and warmed, in order to separate the fatty acids. By similar and well-known methods, the portions of these acids thrown down along with the bird-lime alcohols can be recovered, after separating them as calcium salts from the alcohols and resinoïd substance, and added to the main quantity. The crude fatty acids, which when cold form a soft, brown, solid mass, are dissolved in alcoholic potash and precipitated again with calcium chloride; the calcium precipitate is washed with spirit which removes chlorides and some colouring matter, as well as some of the calcium salt of the soft fatty acid; the precipitate is then washed with ether, as this dissolves out most of the remaining colouring matter and calcium salt of the soft fatty acid more easily than spirit does; lastly, it is heated with hydrochloric acid and water in order to get the crude palmitic acid. On repeating these operations once or twice, and finally crystallising the product from spirit, the palmitic acid is obtained in a pure state. By appropriate treatment, the spirit and ether washings

of the calcium precipitate yield the semi-liquid acid although in an impure condition.

Palmitic acid can also be prepared from bird-lime by destructive distillation. Its purification from hydrocarbons, by means of saponification, presents no great difficulty, and need not be described.

The Alcohols of Bird-lime.

To one of the two alcohols of bird-lime we give the name *mochylic alcohol*, formed from the Japanese word, *mochi*, for (bird-)lime or glutinous matter; and to the other we attach the name *ilicylic alcohol*, essentially the same as *ilicic alcohol*, given by Personne to the single alcohol described by him, but framed more in accordance with the accepted nomenclature for alcohols. Our ilicylic alcohol differs but little from Personne's ilicic alcohol. Both the alcohols of bird-lime are obtained in tufts of small, slender, lustrous prisms, and are distinguishable from each other only in solubility, in melting point, and in composition.

Mochylic alcohol occurs much more abundantly than ilicylic alcohol. It dissolves well in 95—98 per cent. spirit, but is almost insoluble in 80 per cent. spirit. It is very little soluble in light petroleum in the cold, is readily soluble in ether, and dissolves also in concentrated sulphuric acid to which, like bird-lime itself, it imparts a red colour. It melts at 234°, and under atmospheric pressure decomposes at a little below the melting point of zinc, the principal product being a viscid matter, apparently the hydrocarbon to be described among the products of the destructive distillation of bird-lime. In a vacuum, it sublimes slightly at a little above 160°, and freely and entirely near and above its melting point, without decomposing or changing in melting point. Heated with palmitic acid in a sealed tube at 150—160°, it yields a substance indistinguishable from bird-lime in essential properties, a sticky transparent matter, readily soluble in ether, but nearly insoluble in the strongest spirit. Our attempts to obtain mochyl acetate by the action of acetic oxide or chloride have been unsuccessful.

Ilicylic alcohol differs from mochylic alcohol in melting at 172°, and in being moderately soluble in 85—90 per cent., although almost insoluble in 80 per cent. spirit. It begins to volatilise in a vacuum below 150°, and sublimes freely near its melting point in beautiful tufts of needles still melting at 172°. Heated with palmitic acid, it also forms a substance like bird-lime. It fails apparently to yield an acetate, even after long heating at 150—170° with acetic oxide, in which when hot it, as also mochylic alcohol, readily dissolves, partly crystallising out again unchanged on cooling, and partly becoming a

dark viscid matter, not the acetate. Personne found that his ilicic alcohol when treated with acetic oxide yielded a crystalline acetate melting at 204—206°. The melting point of Personne's ilicic alcohol was 175°, and its boiling point above 350°, but under a reduced pressure of 100 mm. it began to sublime at 115°. In appearance and in behaviour to spirit of different strengths, it was like our ilicylic alcohol. Both mochylic and ilicylic alcohols dissolve in a mixture of sulphuric and nitric acids, and from the solution water separates a gelatinous matter, readily soluble in spirit, and deflagrating only slightly when dried and heated.

Chemical Composition of the Two Alcohols.—Combustion of the two alcohols has given us the following results :—

Mochylic Alcohol, m. p. 234°.

	I.	II.	III.	$C_{26}H_{46}O$.
Carbon.....	83·37	83·39	83·28	83·42
Hydrogen ...	12·29	12·16	12·38	12·30
Oxygen.....	—	—	—	4·28
				100·00

Ilicylic Alcohol, m. p. 172°.

	I.	II.	$C_{22}H_{38}O$.
Carbon	83·09	82·98	83·02
Hydrogen	11·93	11·92	11·95
Oxygen.....	—	—	5·03
			100·00

Ilicic Alcohol, m. p. 175° (Personne's Analyses).

	I.	II.	III.	IV.	V.	Mean.	$C_{25}H_{44}O$.
Carbon ..	83·25	83·64	83·48	83·07	83·40	83·36	83·33
Hydrogen	12·18	12·44	12·17	12·24	11·98	12·20	12·22
Oxygen..	—	—	—	—	—	—	4·45
							100·00

It will be seen that Personne's numbers vary rather widely, but fall for the most part between those obtained by us for our two alcohols. It will also be seen that the formula he has proposed, as agreeing best with the mean of his analysis, is that of a homologue of our alcohols, the general expression being $C_nH_{2n-6}O$. As he worked on bird-lime from a species of Ilex different from that which yields Japanese bird-lime, it cannot for the present be decided whether ilicic alcohol is distinct from the alcohols here described.

The Resinoïd Component of Bird-lime.

The resinoïd substance is obtained in pale-yellow fragments, which are brittle, and not sticky like bird-lime. It melts at 110°, and does not volatilise when heated to 220° in a vacuum. Above 360° it darkens, boils, and distils without much apparent change. It is very soluble in spirit, even of 80 per cent. strength, also in ether. When its alcoholic solution is sufficiently evaporated by heat, it separates from its solvent as a viscid liquid, still containing spirit, but this evaporates on further heating below 100°. Its solubility in spirit is not increased by the presence of potassium hydroxide. Heated with the solid hydroxide barely to the melting point, it slowly combines with it, probably at the same time absorbing oxygen. The cooled mass wholly dissolves in water, from which hydrochloric acid precipitates a gelatinous substance, very brittle when dried. We have not further examined it for want of material.

When bird-lime is kept for a long time, a thin brittle skin forms on its surface which is readily soluble in spirit. This skin consists probably of the resinoïd substance. If it does not, then we have no evidence as to whether the resinoïd substance is produced during the saponification of the bird-lime, or exists in it ready formed as the result of slow atmospheric oxidation.

In composition, the resinoïd substance differs from mochylic alcohol only in having two atoms less of hydrogen, as the following analyses and calculation show :—

	I.	II.	$C_{26}H_{44}O$.
Carbon.....	83·79	83·66	83·87
Hydrogen.....	11·80	11·92	11·83
Oxygen.....	—	—	4·30
			100·00

The Fatty Acids of Bird-lime.

The fatty acids of bird-lime are two, as already stated, *palmitic acid*, and, in small quantity only, a semi-liquid acid, the calcium salt of which is soluble in spirit and in ether. This acid has not been further examined. The other shows all the characters of palmitic acid. Melting point, 61·5°. Analysis of (I) acid prepared by saponification, and (II) acid obtained by destructive distillation of purified bird-lime :—

	I.	II.	Palmitic acid.
Carbon.....	74·98	74·86	75·00
Hydrogen	12·67	12·55	12·50
Oxygen.....	—	—	12·50
			100·00

The potassium salt yielded 13·3 per cent. of potassium.

Products of Destructive Distillation.

These have been already enumerated, so far as their nature is known to us, and the result of analysis of the palmitic acid has just been tabulated. The principal hydrocarbon, distilling next after the palmitic acid, was prepared from the middle portion of the distillate by treating it with hot spirit so as to leave about half of it undissolved. This was then washed with cold spirit. The hydrocarbon thus left was a thick oil, slightly yellow but not fluorescent. On analysis it gave numbers agreeing with the formula $C_{26}H_{44}$:—

	Found.	Calculated.
Carbon.....	87·59	87·64
Hydrogen	12·49	12·36
	100·08	100·00

Apparently the same compound is obtained by distilling mochylic alcohol under the ordinary atmospheric pressure. The decomposition of the main constituent of bird-lime by heat may therefore be thus represented:—

$$\text{Mochyl palmitate, } C_{42}H_{76}O_2 = C_{26}H_{44} + C_{16}H_{32}O_2,$$

and the decomposition of mochylic alcohol by—

$$C_{26}H_{46}O = C_{26}H_{44} + H_2O.$$

The last fractions of the distillate consisted of hydrocarbons yielding nearly 91 per cent. of carbon. No attempt was made to isolate the caoutchouc-hydrocarbons no doubt present in the mixture.

Constitution of Bird-lime.

Bird-lime is closely allied to the waxes, and consists principally of *mochyl* and *ilicyl palmitates*, $C_{42}H_{76}O_2$ and $C_{38}H_{76}O_2$.

XXV.—*Chemical Investigation of Wackenroder's Solution, and Explanation of the Formation of its Constituents.*

By Professor H. Debus, Ph.D., F.R.S.

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Introduction.

The milky liquid produced by the action of sulphuretted hydrogen on an aqueous solution of sulphurous acid contains, according to Wackenroder and other chemists, besides free sulphur, a peculiar acid called pentathionic acid. This acid cannot be separated from its solution by distillation or crystallisation, and consequently has not yet been prepared in a pure state. Ludwig could not produce pentathionates, but in place of these he obtained bodies having the composition of double salts of tetra- and penta-thionic acids. Wackenroder, Kessler, and Spring failed, like Ludwig, in their endeavours to produce pentathionates from Wackenroder's solution.

These unsuccessful experiments, together with some positive indi-

cations, which need not be considered in this place, caused Spring to come to the following conclusions:—

1. The so-called pentathionic acid is identical with tetrathionic acid.

2. The reactions, which are described as characteristic of pentathionic acid, are also produced by ammonic tetrathionate.

3. Pentathionic acid is a solution of sulphur in tetrathionic acid, not in atomic proportions, but of the same description as the solution of sulphur in carbon disulphide.

A salt, prepared by Lenoir before the publication of Spring's researches, by adding baric carbonate to a Wackenroder solution, has very nearly the composition of baric pentathionate. This salt is, according to Spring, a mixture of sulphur and baric tetrathionate I do not think that Lenoir, who is known to me as a careful worker, would analyse such a mixture and describe it as a pure compound. But if the substance is not a mixture of baric tetrathionate and sulphur, then it must be baric pentathionate or a mixture of various polythionates of the average composition of a pentathionate.

In order to test the correctness of Spring's views, I suggested to Mr. Lewes, Assistant in the Laboratory of the Royal Naval College, some experiments on the preparation of salts of pentathionic acid. He carried out these experiments with much perseverance and skill, and succeeded in preparing nearly pure potassic and baric pentathionates.

Shaw has repeated some of the experiments of Lewes and confirmed his results. Lewes, however, could not recrystallise his pentathionates, they decomposed into sulphur and tetrathionates.

This decomposition is regarded by Spring as a positive proof that the salts obtained by Lewes are mixtures of tetrathionates and sulphur. Although I did not doubt the interpretation of Lewes, a thorough investigation of the subject appeared to me to be desirable from more than one point of view. It was desirable to prepare pure pentathionates and to examine some reactions of the polythionates of more than ordinary interest.

The compounds usually called acids, like sulphuric acid, H_2SO_4, are regarded in this paper as hydrogen salts, and the name of acid is reserved for the so-called anhydrides. Therefore the dioxide of sulphur, SO_2, is called sulphurous acid, and the compound with water, H_2SO_3, is called hydric sulphite. Hydrogen plays in such compounds the part of a metal.

Correct expression also promotes correct thinking. Polythionates are bodies represented by the formulæ $M_2S_3O_6$, $M_2S_4O_6$, $M_2S_5O_6$, and $M_2S_6O_6$, in which "M" stands for hydrogen or a monovalent metal.

Wackenroder's solution is the liquid obtained by the passage of

sulphuretted hydrogen through an aqueous solution of sulphurous acid until the latter is completely decomposed.

I will, before describing my own experiments, give a list of the papers which have hitherto been published on pentathionic acid and pentathionates.

1. Plessy, "On some New Acids of Sulphur produced by the Action of Sulphur Chloride on Sulphurous Acid" (*Compt. rend.*, **21**, 473; *Ann. Chim. Phys.*, **20**, 162; *Berzelius, Jahresbericht*, **26**, 72; **28**, 24).
2. Th. Thomson, "A New Acid obtained by the Action of Sulphuretted Hydrogen on Sulphurous Acid" (*Ann. Phil.*, **12**, 441).
3. Wackenroder, "On Pentathionic Acid" (*Archiv der Pharmacie*, **48**, 272, 140; *Berzelius, Jahresbericht*, **27**, 36).
4. Lenoir, "On Baric Pentathionate" (*Annalen der Chemie und Pharmacie*, **62**, 253; *Berzelius, Jahresbericht*, **28**, 21).
5. Ludwig, "On Potassic and Baric Tetrapentathionate" (*Archiv der Pharmacie*, **51**, 259; *Berzelius, Jahresbericht*, **28**, 108).
6. Fordos and Gélis, "Action of Sulphur Chlorides on Sulphurous Acid" (*Ann. Chim. Phys.*, **22**, 66; **28**, 451; *Berzelius, Jahresbericht*, **29**, 13).
7. Kessler, "On Polythionates" (*Poggendorff Ann.*, **74**, 249; *Berzelius, Jahresbericht*, **29**, 15).
8. Sobrero and Selmi, "On the Action of Sulphuretted Hydrogen on Sulphurous Acid" (*Ann. Chim. Phys.*, **28**, 210; *Liebig's Jahresbericht*, **3**, 264).
9. Risler-Bennet, "Formation of Pentathionic Acid by the Action of Zinc on Sulphurous Acid" (*Poggendorff Ann.*, **116**, 470).
10. Chancel et Diacon, "Conversion of Penta- into Tetra-thionic Acid" (*Compt. rend.*, **56**, 710).
11. Rammelsberg, "Potassic Pentathionate" (*Liebig's Jahresbericht*, **10**, 136).
12. W. Spring, "Contributions to our Knowledge of the Polythionic Acids" (*Berichte der deutschen chemischen Gesellschaft*, **6**, 1108). "On the Non-existence of Pentathionic Acid" *Liebig's Annalen*, **199**, 97; **213**, 329).
13. Stingl and Morawski (*Liebig's Jahresbericht* (1879), 1110).
14. Takamatsu and Smith, "On Pentathionic Acid" (*Journal of the Chemical Society*, **37**, 592; **41**, 162).
15. Lewes, V., "On Pentathionic Acid" (*Journal of the Chemical Society*, **39**, 68; **41**, 300).
16. Curtius, "Experiments with the so-called Pentathionic Acid" (*Jour. prakt. Chemie* [2], **24**, 225).

17. Shaw, "On the Preparation of Pentathionates" (*Journal of the Chemical Society*, **43**, 351).
18. Smith, "Note on Pentathionic Acid" (*Journal of the Chemical Society*, **43**, 355).
19. Salzer, "On a New Mode of Formation of the so-called Pentathionic Acid (*Berichte der deutschen chemischen Gesellschaft* (1886), 1696).

A. Composition of Wackenroder's Solution.

I. *Preparation.*

A slow current of sulphuretted hydrogen is passed for two hours through 480 c.c. of a nearly saturated solution of sulphurous acid at a few degrees above 0° C. The liquid, which must still contain a large excess of sulphurous acid, is now kept for 48 hours in a closed bottle at common temperatures. The operation is then repeated, a current of hydric sulphide is again passed for two hours, and the liquid allowed to remain at rest for two days.

The treatment in this manner is continued till all the sulphurous acid is decomposed; about two weeks are necessary for the accomplishment of this purpose. Certain precautions have to be observed if the end of the operation is to be recognised by the disappearance of the odour of the sulphurous acid. If the current of hydric sulphide is discontinued as soon as the liquid ceases to smell of sulphurous acid, and the bottle is then taken out of the cold water by which it is surrounded and is allowed to stand for a few hours at common temperatures, the liquid will again assume an intense odour like sulphurous acid. The treatment with sulphuretted hydrogen must then be repeated, and is only regarded as complete when after standing for several hours at common temperatures the solution no longer smells like sulphurous acid. The liquid so prepared is of milky appearance and contains a large precipitate of sulphur which is separated by filtration. The filtrate is, however, not clear and cannot be obtained clear by filtration because it contains in suspension a considerable quantity of sulphur in very small particles which will pass through the best Swedish filtering-paper. In a bottle of about an inch in diameter it appears semi-transparent, in transmitted light of a reddish-brown colour, becoming more transparent on warming and more opaque on cooling.

Our problem now will be to determine the composition of this liquid. We shall have to separate the substances contained in the solution and ascertain their nature, and after completing this task we shall have to explain their formation from the original material, water, sulphurous acid, and sulphuretted hydrogen.

The experiments described in this paper prove that Wackenroder's solution contains the following substances:—

a. Small drops of sulphur in suspension.
b. Sulphur in solution, in the colloidal condition, similar to silica dissolved in diluted hydric chloride. Sulphur in this condition forms a new, hitherto unrecognised, allotropic modification.
c. Hydric sulphate.
d. Traces of hydric trithionate.
e. Hydric tetrathionate.
f. Hydric pentathionate.
g. A polythionate with more sulphur than a pentathionate, probably hydric hexathionate.

II. *Examination of the Sulphur which separates as a Precipitate during the Passage of Sulphuretted Hydrogen through the Solution of Sulphurous Acid.*

The greater mass of this sulphur is of a soft, gummy nature, and forms with water an emulsion in which drops of sulphur can be seen under the microscope. A portion of it is, however, present in the ordinary modifications, in hard, brittle particles, and mixed with these are observed elastic membranes. The latter were, probably, formed by adhesion of liquid sulphur to the sides of the vessel and gradual hardening of the layer into a mass like caoutchouc. The emulsion formed by the soft plastic portion with water cannot be rendered clear by filtration. If it is diluted with much water, a brown-yellow semi-transparent liquid is obtained from which a solution of saltpetre throws down a copious precipitate of sulphur.

III. *Examination of the filtered Wackenroder Solution.*

The milky fluid does not become clear even after standing two or three weeks in a quiet place. A drop observed under the microscope appears homogeneous, but after about five minutes a ring of yellow particles appears round the edge of the drop, and grows by degrees towards the centre. This deposit is seen to be composed of minute *drops* of sulphur. The quantity so separating is evidently much larger than the amount in suspension, consequently, a precipitation of dissolved sulphur has taken place. The addition of a little water causes this precipitated sulphur to dissolve. The filtered Wackenroder solution contains rather large quantities of sulphur in simple solution, as colloidal sulphur in a new allotropic modification, which I will distinguish as "δ" sulphur. The solution of δ-sulphur resembles the solution of silica in dilute hydric chloride. A drop of

the Wackenroder solution left on a piece of glass evaporates, and dissolved sulphur, corresponding to the amount of evaporation, separates in the liquid state.

A larger portion of the Wackenroder solution was now evaporated under the receiver of an air-pump over pieces of potassic hydroxide. Considerable quantities of sulphur in a viscous semi-fluid condition, separated as the solution became more concentrated. The surface of the evaporating liquid looked as if a layer of oil was floating on it, and at the sides of the basin a yellow shining coating like varnish was observed. The liquid became clear and transparent, in layers of $2\frac{1}{2}$ inches in thickness, after about $\frac{2}{3}$ of it had evaporated, and appeared slightly opalescent, like a solution of albumin. In this condition, however, it still contains much δ-sulphur in solution, because further evaporation, addition of hydric chloride, sodic chloride, baric chloride, saltpetre, cupric sulphate, and other salts, respectively, cause the precipitation of considerable quantities of sulphur. The same effect but in less degree is likewise observed when the concentrated solution is kept in a closed bottle in a dark place.

About 100 c.c. were divided into three equal portions. The second portion was mixed with twice its volume of water, and the third with twice its volume of an aqueous solution of sulphurous acid. After standing 21 days, a deposit of sulphur in each of the three portions had taken place. The smallest deposit was in the second, and the largest in the third.

Water retards, sulphurous acid accelerates the precipitation of δ-sulphur. A Wackenroder solution was saturated with sulphurous acid, and allowed to remain in a closed bottle for a few days. It became perfectly clear, both the suspended and the dissolved δ-sulphur falling down as a precipitate.

Experiments were now made to separate from Wackenroder's solution, which had been so far concentrated as to appear clear and transparent in layers of 2 inches in thickness, the dissolved δ-sulphur by means of diffusion, and thus to obtain a pure aqueous solution of sulphur.

A porous cell, like those used in galvanic batteries, was immersed for a few days in dilute hydric chloride in order to remove alkalis and other soluble substances, and then well washed with water. Wackenroder's solution was placed in this cell, and the latter in a large vessel containing water. The acid of the solution rapidly diffused through the porous clay, but the coagulation of the sulphur began and was completed before all the acid had diffused. A second experiment made in the same manner, as well as a third made with parchment paper, failed in the same way.

The sulphur, which had separated during the evaporation of the

filtered Wackenroder solution, was collected on a filter. The particles united in the course of the night into one semi-transparent lump, of the appearance of wax and of a gummy, sticky nature. In another experiment, the sulphur separated in a more fluid condition. The filter on which it had been collected was placed upon blotting-paper. Some of the sulphur, like oil, was absorbed by the paper after the evaporation of the water. A little of this sulphur was mixed with some clear Wackenroder solution, and a drop of the mixture placed under the microscope. The sulphur was partly seen in minute transparent drops, and partly in irregularly formed masses, rounded off at the edges. The remaining sulphur on the filter could not be purified by washing with water. Much of it passed with the water through the filter, and formed an emulsion resembling the original Wackenroder solution; only drops of sulphur could be seen in this emulsion under the microscope, and after a few hours a sediment of drops separated. A portion of the emulsion was allowed to remain in a bottle at rest from June to December. It was still of the nature of an emulsion, a precipitate could be observed, but the liquid above this precipitate was not clear.

Carbon disulphide, benzene, ether, olive oil, chloroform, or tannin did not clear the liquid, but powder of charcoal, baric carbonate alkalis, a concentrated solution of hydric chloride, hydric nitrate, and potassic nitrate caused complete precipitation of the sulphur in suspension and solution. Addition of much water caused the emulsion to become almost clear; at least, in layers of an inch in thickness, it appeared perfectly clear, transparent, and slightly yellow. Solution of saltpetre produced in this diluted clear liquid a copious precipitate of sulphur. The drops of sulphur in suspension in the emulsion appear, therefore, to be soluble in much water.

Another portion of the said emulsion was allowed to evaporate under the exhausted receiver of an air-pump over hydric sulphate. The sulphur remained as a thin elastic membrane resembling caoutchouc. This membrane did not again form an emulsion with water, neither did alcohol appear to produce any effect on it, but carbon disulphide dissolved a portion and took away its elasticicy.

Some sulphur, which had separated during the evaporation of Wackenroder's solution over potassic hydroxide in the exhausted receiver of an air pump, and which was of the same plastic, gummy nature as the sulphur described above, was placed in some water, in which it dissolved, forming a turbid solution. The dissolved portion was reprecipitated by addition of sodic chloride, then filtered, and the filtering-paper with the precipitate placed on blotting-paper; the adherent aqueous solution passed into the paper, and the remaining sulphur was then mixed with water, with which it formed an

emulsion, and from this was again precipitated by a solution of common salt.

The sediment was again collected on and pressed between layers of bibulous paper, and after these operations put in water, in which a portion of it dissolved. After two or three filtrations an almost clear opalescent liquid, similar to a solution of albumin, was obtained. The filtrate became quite clear on warming and more turbid on cooling. Red and blue litmus-papers were not affected by it. A piece of bright silver foil immersed in it turned black by degrees. Sodic chloride, hydric chloride, alkalis, saltpetre, and baric carbonate respectively, caused the formation of a precipitate of sulphur. The same effect was produced by recently precipitated baric sulphate. Ammonia produced no change. Some of the filtrate evaporated on a watch-glass left a viscous, transparent residue. I conclude from these experiments that a great part of the sulphur which separates during the evaporation of a Wackenroder solution is soluble in much water, or, more correctly, in water which contains a little acid or a very little common salt.

We are now able to explain why a Wackenroder solution, which contains sulphur in minute drops in suspension, and possesses the character of an emulsion, will not become clear even if it is allowed to stand for months in a closed bottle in a quiet place. We prepare emulsions by mixing intimately oil with gum, albumin, or other colloïds and water. The minute drops of oil are prevented by the colloïd from uniting and separating as a layer on the surface of the water. A colloïd cannot diffuse through a membrane formed of another colloïd, perhaps because the molecules are too large and sluggish in their motions. In the case of an ordinary emulsion, the large, sluggish molecules of the colloïd place themselves between the drops of oil, impede their motion, and thus prevent their union. Now the sulphur which is in solution in the Wackenroder liquid acts like a colloïd, as gum or albumin in an ordinary emulsion, and prevents the union of the minute drops of sulphur which are in suspension in the liquid. The Wackenroder solution loses the character of an emulsion as soon as the dissolved sulphur is removed.

Sulphur separates as a precipitate if Wackenroder's solution is kept for some time or if it is evaporated. But however the separation is effected, the precipitated sulphur is far less soluble than it was before its coagulation. In the beginning of the evaporation, when the liquid is less acid, the sulphur separates in a more liquid and soluble condition, whereas later on, when the Wackenroder solution becomes more concentrated, the precipitated sulphur is harder and more brittle, in fact is made up in a great measure of the ordinary modifications. Also the temperature of evaporation has an influence

on the condition of the sulphur. At lower temperatures, a larger proportion of liquid, soluble sulphur is separated than at higher temperatures.

It will be understood from these remarks that the sulphur which separates during evaporation from a Wackenroder solution is a mixture of different modifications. Besides δ-sulphur, which forms an emulsion and dissolves in much water, it contains ordinary sulphur, for if it is treated with alcohol δ-sulphur is dissolved, and the remaining portion contains small rhombic octahedra. On the other hand, bisulphide of carbon will extract octahedral sulphur and leave the amorphous behind.

It appears, according to my observations, that δ-sulphur, if kept very long, becomes gradually converted into hard, brittle sulphur. However, I have made no special experiments on this point.

The properties of soluble colloïdal sulphur suggest the following method for its preparation. A current of sulphuretted hydrogen is passed through not more than 120 c.c. of an aqueous solution of sulphurous acid at a few degrees above 0° C., until all the sulphurous acid is decomposed. The liquid is then filtered, and concentrated over pieces of potassic hydroxide in the exhausted receiver of an air-pump. The evaporation is stopped as soon as the liquid commences to become clear, and the precipitated sulphur is collected on a filter.

If we take a retrospective view of the properties of the sulphur as it is contained in solution in Wackenroder's liquid, and can be obtained from it by partial evaporation, we find that it possesses all the properties which Graham* describes as characteristic of the colloïds.

The sulphur dissolved in Wackenroder's solution does not diffuse through porous clay or parchment. It is held in solution by very feeble force. Slow and gradual separation takes place when its solutions are kept for some time, or complete precipitation, if apparently inert substances, such as sodic chloride, charcoal powder, or baric sulphate, are added. The unstable condition of its molecules, their slow change into other modifications, and finally its gummy, sticky condition remind one of the colloïds.

The chemical powers are likewise very feeble. Sulphur can combine with hydric tetrathionate, and form hydric pentathionate, and although large quantities of both sulphur and hydric tetrathionate are in Wackenroder's solution they do not combine, but seem to be inert towards each other.

All this points to the conclusion that we have to deal with a new allotropic modification of sulphur.

* *Chemical and Physical Researches.* Collected by James Young, pp. 593—596.

Wackenroder's solution can be concentrated on a water-bath without decomposition until it reaches the sp. gr. 1·32. The δ-sulphur is all coagulated before it reaches this point of concentration. Further evaporation on the water-bath causes evolution of sulphurous acid and precipitation of sulphur. In a partial vacuum, over pieces of potassic hydroxide, at common temperatures, I have concentrated it to the sp. gr. 1·46 without decomposition. In this concentrated condition it is usually described in the text-books as pentathionic acid, $H_2S_5O_6$. A small quantity, which had been left for some time under a bell-jar over pieces of potassic hydroxide, had evaporated to dryness. The dry residue was amorphous and intermixed with crystals. A few drops of water dissolved the amorphous portion and left beautiful small octahedral crystals of sulphur. The aqueous solution showed the reactions of a pentathionate. (See Potassic Pentathionate.)

From this observation, it seems to follow that hydric pentathionate can exist in the solid form. Wackenroder's solution of the sp. gr. 1·46, is a colourless, transparent, oily liquid of great refractive power and intensely acid. It destroys the coherence of the fibres of filtering-paper, and can only be filtered when of lower sp. gr. than 1·4.

A sample of 1·3 sp. gr. I have kept in a closed bottle in a dark place for three months without apparent change, then a slow decomposition set in with evolution of sulphurous acid and precipitation of sulphur, a decomposition which was not completed in two years.

Wackenroder's solution is, apparently for two reasons, described in the text-books as hydric pentathionate:—

1. Kessler described three reactions of this liquid which hydric tri- and tetra-thionate do not give; and—

2. He found that the acid of the solution contained sulphur and oxygen in the ratio of 5 : 5.

Before I repeated the analysis of Wackenroder's solution, I first investigated Kessler's analytical method. This chemist found that potassic tetrathionate and mercuric cyanide decompose at 100°, as represented by the following equations:—

$$HgCy_2 + K_2S_4O_6 = 2KCy + HgS_4O_6, \text{ and}$$
$$HgS_4O_6 + 2H_2O + 2KCy = HgS + S + 2KHSO_4 + 2HCy.$$

If instead of potassic tetrathionate a Wackenroder solution is taken, the same products of decomposition are obtained, only with this difference, that in place of potassic hydric sulphate we have hydric sulphate, and in the precipitate instead of 1 atom of mercury and 2 of sulphur, 1 atom of the metal and 3 of sulphur.

From these results, the conclusion has been drawn that Wackenroder's solution contains an acid similar to tetrathionic acid with 5 atoms of sulphur in 1 molecule.

Takamatsu and Smith, and also Lewes, have confirmed the above results of Kessler. It is, however, desirable to test Kessler's method with a pure pentathionate, which hitherto has not been done.

Potassic pentathionate should be decomposed according to the following equation:—

$$K_2S_5O_6 + HgCy_2 + 2H_2O = 2KHSO_4 + HgS + S_2 + 2HCy.$$

If, therefore, the amount of sulphate in solution and the quantity of mercury and sulphur in the precipitate be determined, from the numbers so obtained, the composition of the pentathionate can be calculated.

The preparation of potassic pentathionate will be described in another part of this paper. A sample of very pure salt was employed in the experiments. The mercuric cyanide was bought as pure in the market. Afterwards, whilst using it, I discovered the presence of mercuric chloride in it. The error caused by this impurity was duly corrected. 0·703 gram crystallised potassic pentathionate was boiled with a solution of mercuric cyanide. 0·773 gram of a black precipitate was produced. 0·677 gram of the latter yielded on treatment with bromine-water 0·118 gram of pure sulphur, and on addition of baric chloride to the filtrate from the sulphur 0·311 gram of baric sulphate. The filtrate from the baric sulphate gave with hydric sulphide 0·547 gram of mercuric sulphide. The filtrate from the precipitate produced with mercuric cyanide at 100°, gave with baric chloride 0·917 gram of baric sulphate.

According to these numbers, we obtain for the composition of the black precipitate caused by mercuric cyanide—

Sulphur	0·183
Mercury	0·538
Chlorine	0·052
	0·773

The difference obtained by the subtraction of the weights of the sulphur and mercury from the weight of the precipitate, represents the weight of the chlorine which was present in combination with mercury and sulphur as mercuric sulphochloride.

Mercury	0·392
Sulphur	0·183
Mercuric chloride	0·198
	0·773

The amount of sulphuric acid corresponding to 0·917 gram of baric sulphate contains the rest of the sulphur, and all the oxygen of

the potassic pentathionate. Adding this amount, 0·315 gram, to the above mercury and sulphur, we obtain the weight of the mercuric pentathionate corresponding to the weight of potassic pentathionate taken = 0·890 gram. Replacing the mercury, 0·392 gram, by its equivalent of potassium, 0·152 gram, we obtain 0·650 gram of potassic pentathionate, which would combine with 0·0525 gram of water forming 0·7025 gram of the crystallised salt, instead of 0·703 gram, the amount actually taken.

In 100 parts we have—

	Found.	Calculated according to $2K_2S_5O_6 + 3H_2O$.
Sulphur.....	44·01	44·32
Oxygen.....	26·92	26·59
Potassium.....	21·65	21·60
Water.....	—	7·48
		99·99

The calculated composition of the potassic pentathionate has been proved to be correct by other methods which will be described in another part of this paper; Kessler's method, therefore, yields accurate results.

A sample of Wackenroder's solution of the sp. gr. 1·46 was diluted with four times its volume of water, and the clear slightly yellow liquid used in the following experiments:—

I. *Determination of Dissolved Sulphur.*

10 c.c. mixed with solution of saltpetre gave 0·005 gram of sulphur.

II. *Determination of Hydric Sulphate.*

10 c.c. gave with baric chloride 0·243 gram of baric sulphate.

III. *Determination of the Sulphur and Oxygen of the Polythionates.*

10 c.c. boiled with mercuric cyanide, which contained also a little chloride, gave 2·875 grams of mercuric sulphochloride and sulphur. The filtrate gave with baric chloride 3·882 grams of baric sulphate. Subtracting the baric sulphate found previously (II), we have for the remaining weight 3·639 grams, corresponding to 0·499 gram of sulphur and 0·750 gram of oxygen as derived from the polythionates of the Wackenroder solution. 0·868 gram of the mercuric sulphochloride and sulphur precipitate treated with bromine-water gave 0·024 gram of sulphur, and the filtrate on addition of baric chloride gave 1·430 gram of baric sulphate. The filtrate from the baric sulphate

yielded with hydric sulphide 0·694 gram of mercuric sulphide. 0·997 gram of the mercuric sulphochloride and sulphur precipitate burnt with plumbic chromate, and metallic copper in the front part of the tube, gave 0·683 gram mercury, but no water or carbonic acid.

According to these data, 2·875 grams of precipitate composed of mercuric sulphochloride and sulphur contain, after the subtraction of the mercuric chloride and the sulphur which existed in Wackenroder's solution free, and was precipitated by saltpetre, (I) 0·724 gram of sulphur and 1·494 gram of mercury. If the sulphur of this precipitate, 0·724 gram, is added to the sulphur of the sulphuric acid, produced by boiling with mercuric cyanide, 0·499 gram, we obtain the sulphur of the polythionates = 1·223 gram, and if we add to this sulphur the oxygen of the polythionates, 0·750 gram, present in the sulphate obtained by boiling with mercuric cyanide, and the hydrogen equivalent to 1·494 gram of mercury, we obtain the composition of the polythionates of Wackenroder's solution—

Sulphur	1·223
Oxygen	0·750
Hydrogen	0·015
	1·988

Or in 100 parts—

	Found.	Calculated. $H_2S_5O_6$.
Sulphur.....	61·52	62·01
Oxygen	37·72	37·21
Hydrogen	0·75	0·77
	99·99	99·99

And the atomic ratio—

$$H : S = 2 : 5{\cdot}12$$

From these experiments, it seems to follow that Wackenroder's liquid is really a solution of pentathionic acid, and as Kessler, Takamatsu and Smith, and Lewes, obtained nearly the same numbers, the probability of this conclusion is thereby increased. If a substance is obtained under different conditions and at different times of the same quantitative composition, it is probably a pure compound. Nevertheless, another interpretation may be given to the analytical results. Wackenroder's solution may be a mixture of an equal number of molecules of tetrathionic acid and the unknown hexathionic acid:—

$$H_2S_6O_6 + H_2S_4O_6 = 2H_2S_5O_6,$$

and if it has this composition it would, if analysed by Kessler's

method, yield numbers agreeing with the composition of pentathionic acid. In order to ascertain which of these two interpretations is correct, I prepared and examined some of the salts which can be formed by the acid or acids of Wackenroder's solution with metals.

Potassic Pentathionate.

Kessler attempted the preparation of this salt but obtained only a mixture of tetrathionate and sulphur. Ludwig divided a Wackenroder solution into two equal parts, neutralised one part with potassic carbonate and added the other part. The solution gave on evaporation crystals of the composition $K_4S_5O_{12},H_2O$, which Ludwig regarded as a compound of potassic tetrathionate and pentathionate. Rammelsberg measured the crystals of a salt which he called potassic pentathionate, but as the mode of preparation, the properties, and the analysis are not described, it remains doubtful whether the salt was a penta- or tetra-thionate.

The first chemist who prepared nearly pure potassic pentathionate was Lewes. He added by degrees to a portion of Wackenroder's solution about half the quantity of potassic hydroxide which would be required for its complete neutralisation. Sulphur was precipitated during this operation, and the filtrate from the precipitate gave, by spontaneous evaporation, crystals of hydrated potassic pentathionate.

The following experiments were made with a Wackenroder liquid of 1·19 sp. gr., of which 5 c.c. required for neutralisation 8·2 c.c. of a solution containing 13·8 per cent. of potassic hydroxide. The solution of potassic hydroxide was added drop by drop with constant stirring to 25 c.c. of Wackenroder's liquid until the acid was nearly neutralised. Much sulphur was precipitated and some sulphurous acid produced. The liquid which was still acid was filtered and allowed to evaporate spontaneously. Sulphur separated again whilst the exaporation proceeded and had to be removed two or three times. At last crystals, not of potassic pentathionate but of potassic trithionate, were formed. This negative result seems to show that the pentathionic acid of the Wackenroder solution has been decomposed during the neutralisation or subsequent evaporation.

One drop of a solution of potassic hydroxide causes *immediately* a precipitate of sulphur in a solution of potassic pentathionate. This salt cannot exist in alkaline solutions. The addition of potassic hydroxide to an acid solution in the ordinary way, even by constant stirring, will cause for moments in certain parts of the mixing liquids an alkaline reaction, and consequent decomposition in case of pentathionic acid. As the addition of the base proceeds, and the amount

of free acid becomes smaller, transient alkalinity will be more frequent and of longer duration, and consequently the more considerable the decomposition. From these considerations, it seems to follow that in order to prevent as much as possible the decomposition of the pentathionate, the Wackenroder liquid ought to be concentrated, the potassic hydroxide very dilute, the mixing of the two as rapid as possible, and finally not more of the base ought to be added than is required for the neutralisation of about half of the acid present. The experiments confirm this conclusion. No pentathionate could be obtained by Ludwig's method, a method which was also adopted by Spring.

These chemists divided Wackenroder's solution into two equal parts and neutralised one part completely. This cannot be done without producing transient alkalinity in parts of the mixing liquids and decomposition of the pentathionate. If the other part of Wackenroder's solution is added and the united liquids concentrated no crystals of pentathionate are obtained. Lewes could prepare the potassic pentathionate because he added to a given quantity of Wackenroder's solution only half the amount of potassic hydroxide required for its neutralisation, so that the base nearly always met an excess of acid.

Kessler has by means of his analytical method determined the quantity of polythionic acids in Wackenroder's solution of given sp. gr. The following are his results:—

Specific gravity.	Percentage of S_5O_5.
1·233	32·1
1·32	41·7
1·47	56·0
1·506	59·7

By means of these numbers, the quantity of potassic hydroxide to be added to Wackenroder's solution of given strength can approximately be calculated. 100 c.c. of a liquid of 1·283 sp. gr. would contain according to my estimate 48·6 grams of acid (S_5O_5), and would require 22·5 grams of potassic hydroxide for neutralisation.

A solution of 6 grams of potassic hydroxide in 100 c.c. of water was sucked into a pipette with a very narrow aperture at its lower end and using the pipette as a stirring rod, were allowed to run into 50 c.c. of Wackenroder's solution of 1·283 sp. gr. As the end of the stem of the pipette moved through the acid the weak solution of potassic hydroxide ran slowly out, and always met a large excess of acid. In this manner very little sulphur was precipitated, indicating that very little, if any, potassic pentathionate had been decomposed. The mixture was now filtered and allowed to concentrate in a partial

vacuum over pieces of potassic hydroxide. After two days' evaporation, a crust of prismatic crystals had formed. This crust, weighing 4·6 grams, was removed and the mother-liquor put back into the vacuum. Two more crops of crystals were obtained, the first weighing 6·2 and the second 1·5 grams. As the crystals of these three separations appeared to be of the same shape, they were united and recrystallised.

Lewes could not at first recrystallise potassic pentathionate, the salt decomposed with separation of sulphur. Fordos and Gélis observed, long ago, that the polythionic acids are more stable in presence of other acids. This observation as well as the conditions under which crystals of potassic pentathionate are obtained from Wackenroder's solution suggested to Mr. Lewes a method of recrystallisation which proved very successful. He dissolved the potassic pentathionate in water which was acidulated with a little sulphuric acid, and observed that the crystals could be reproduced from this solution.

I took 50 grams of water acidulated with 0·66 gram of hydric sulphate, and introduced into this liquid at 50° the 12·3 grams of crystals obtained as before described. All dissolved except a few milligrams of sulphur which were separated by filtration. The filtrate was run into a glass dish with a flat bottom and allowed to concentrate by spontaneous evaporation. As the solution became stronger, two descriptions of well-developed crystals, some of them $\frac{3}{8}$ of an inch in diameter, separated from the liquid. Six-sided prisms with pyramids only on one end, and with the side on which they were resting much developed, could easily be distinguished from four-sided rhombic or six-sided star-like plates. The first were found to be potassic tetrathionate and the second potassic pentathionate. The latter is also sometimes obtained in short, thick prisms with more or less developed pyramids. It is the enlargement of two sides of these prisms parallel to the chief axis and opposite to each other which causes them to appear sometimes like six-sided plates. Both descriptions of crystals were placed on blotting-paper, and after they were dry, the potassic pentathionate could easily be picked out from the mixture; its weight was 4·2 grams. Both the potassic penta- and tetra-thionate were recrystallised a second time from water acidulated with hydric sulphate. 50 c.c. of Wackenroder's solution of 1·283 sp. gr. yielded in this way 12·3 grams of a mixture of potassic tetra- and penta-thionate, and this mixture was resolved by two crystallisations into 2·25 grams of very pure potassic pentathionate, and 4·0 grams of potassic tetrathionate.

The yield by this method of preparation is not good, as at least half of the pentathionic acid of Wackenroder's solution remains in the original mother-liquor. I was fortunate enough to find a method

generally applicable, by means of which every pentathionate which will crystallise can be prepared without loss of pentathionic acid. The principle of the method will be understood from the following description.

The acids of Wackenroder's solution are strong and not volatile. If mixed with an acetate, the hydrogen of the polythionates, $H_2S_5O_6$, $H_2S_4O_6$, is exchanged for metal, producing metallic polythionates and hydric acetate. The latter evaporates if the mixture is exposed to the atmosphere. These operations can be performed *without decomposition* of the pentathionates.

43 c.c. of Wackenroder's solution of 1·343 sp. gr. contain according to my calculation (see page 292) 24 grams of pentathionic acid (S_5O_6) and would according to the following equation—

$$H_2S_5O_6 + 2KC_2H_3O_2 = K_2S_5O_6 + 2C_2H_4O_2,$$

require 19·8 grams of potassic acetate for the formation of potassic pentathionate and hydric acetate. I took a little less, only 16·66 grams of previously fused potassic acetate, dissolved it in the smallest quantity of water, and acidulated with a few drops of hydric acetate. This solution was now mixed with 43 c.c. of Wackenroder's liquid of sp. gr. 1·343. The mixture measured 85 c.c., and was put on a large plate, so as to present a great surface to the atmosphere, and then placed in the window of a small draught closet, in order to cause a constant current of air to pass over the surface of the mixture. The acetic acid and water evaporated in 24 hours and left a white crystalline residue which was repeatedly pressed between layers of Swedish filtering-paper. This residue (26 grams) dissolved in 50 c.c. of water acidulated with 1 c.c. of hydric sulphate, at 40° C., leaving only about 0·005 gram of sulphur behind. The sulphur was separated by means of a filter, and the filtrate, which did not smell of acetic acid, left to spontaneous evaporation in a vessel with a flat bottom. The crystallisation commenced on the following day and yielded 18·75 grams of very fine crystals of a mixture of potassic tetra- and penta-thionate, instead of only 12 grams as in the previous experiment. Some of the crystals were $\frac{1}{3}$ of an inch in diameter. 5·75 grams of potassic pentathionate could be picked out of the mixture. The remaining 13 grams as well as the 5·75 grams of pentathionate were each by itself twice recrystallised from water acidulated with a little hydric sulphate. For 1 gram of salt, 2·25 grams of water and 0·02 gram of the acid were taken.

The crystals obtained were large and well developed, so that the pentathionate could easily be separated from the potassic tetrathionate. In this manner, 5 grams of very pure potassic pentathionate

and 6·35 grams of pure potassic tetrathionate were obtained. The yield is more than twice as great as in the previous experiment.

The use of potassic acetate in place of potassic hydroxide is therefore highly advantageous, because all the acid of Wackenroder's solution can be converted into the potassium salt, and the hydric acetate which is set free tends to prevent the decomposition of the potassic pentathionate. The pentathionates of the heavy metals can only be produced by the addition of the acetates of the metals to Wackenroder's solution.

The mother-liquors of the crystals mentioned above still contained much potassic pentathionate and tetrathionate; they can easily be recovered by adding for every molecule of sulphuric acid used 2 mols. of potassic acetate and evaporating to dryness at common temperatures. The residue of polythionates and sulphate is then treated in the same way as the original crystals.

Potassic pentathionate is obtained quite pure by crystallisation from water acidulated with hydric sulphate. But it is also possible to crystallise the salt from pure water. 40 grams of water were heated to 50°, and then potassic pentathionate in powder was introduced by degrees until the liquid was nearly saturated. The solution was now passed through a filter into a beaker.

The crystallisation commenced almost immediately, and proceeded so rapidly that one could see the lighter mother-liquor rise from the newly-formed crystals towards the surface of the solution. About one or two hours after the latter had assumed the temperature of the room, the mother-liquor was poured off a crop of very fine prisms, some $\frac{1}{3}$ of an inch in length. The salt remaining in the mother-liquor can be recovered by precipitation with alcohol, but not by evaporation, because it decomposes into tetrathionate and sulphur.

This decomposition occurs even if a concentrated solution is left standing for several hours. The crystals of potassic pentathionate cannot be kept long. In the course of a month or two, yellow points are observed in them, these points grow and increase in number, until the whole crystal is turned into a yellow, pulpy mass consisting chiefly of water, potassic tetrathionate, and sulphur. The cause of this spontaneous decomposition is the presence of water contained in cracks and fissures of the crystals. In order to preserve the salt, the crystals must be rubbed to a fine powder and the latter washed with dilute alcohol. In this state, I have kept the salt over hydric sulphate in an exsiccator for two or three years without the slightest change.

Analysis of Potassic Pentathionate.

A. Crystallised from pure water. 0·662 gram were oxidised with hydric nitrate and the excess of the latter removed by evaporation

with hydric chloride. On addition of baric chloride, 2·084 grams of baric sulphate were precipitated. 0·972 gram of the same salt gave 0·471 gram potassic sulphate.

II. 0·518 gram were treated with bromine-water and the excess of bromine evaporated on the water-bath. 0·045 gram of sulphur remained undissolved; the filtrate from this sulphur gave with baric chloride 1·3565 gram of baric sulphate. The bromine used in this experiment was proved to be pure. 0·931 gram of the substance was evaporated with pure hydric sulphate and heated to redness. The weight of the residue was 0·448 gram.

B. Potassic pentathionate prepared by the addition of potassic hydroxide to Wackenroder's solution and crystallisation from water containing hydric sulphate.

III. 0·701 gram was oxidised with bromine-water and the undissolved sulphur washed with dilute ammonia. 0·114 gram of sulphur was obtained, and 1·405 gram of baric sulphate by precipitation with baric chloride. 1·598 gram of the substance heated to redness left 0·770 gram of potassic sulphate. 2·931 grams burnt with plumbic chromate in a combustion-tube gave 0·2265 gram of water.

IV. Potassic pentathionate prepared by Mr. Lewes and analysed by Mr. Cowper. 0·4895 gram gave 0·235 gram of potassic sulphate. 0·5045 gram gave 1·6175 gram of baric sulphate. 0·7205 gram gave 0·057 gram of water.

C. Potassic pentathionate obtained by the addition of potassic acetate to Wackenroder's solution and crystallisation from water containing hydric sulphate.

V. 0·541 gram oxidised with bromine-water and the solution precipitated with baric chloride gave 1·741 gram of baric sulphate. 0·453 gram heated to redness left 0·221 gram of potassic sulphate.

Percentage Composition.

	I.	II.	III.	IV.	V.	Theory. $2K_2S_5O_6 + 3H_2O$.
Potassium..	21·70	21·57	21·58	21·54	21·80	21·60
Sulphur....	43·23	44·61	43·76	44·03	44·20	44·32
Oxygen....	—	—	—	—	—	26·59
Water	—	—	7·72	7·91	—	7·48
						99·99

The atomic ratios are—

I. K : S = 2 : 4·85
II. K : S = 2 : 5·04
III. K : S = 2 : 4·94
IV. K : S = 2 : 4·97

Potassic pentathionate dried over hydric sulphate has, consequently, the formula $2K_2S_5O_6,3H_2O$.

Lewes mentions three salts, $K_2S_5O_6$, $K_2S_5O_6,H_2O$, and $K_2S_5O_6,2H_2O$. Shaw calculated from his numbers the formula $K_2S_5O_6{\cdot}H_2O$.

The salts prepared by Lewes and Shaw were not recrystallised, but were analysed in the same state in which they separated from the original solution. I believe they were not quite pure. If we consider the hydrogen of the water of crystallisation replaced by potassium in the formula $2K_2S_5O_6,3H_2O$, we have the composition of 5 mols. of potassic thiosulphate.

The crystalline forms of potassic pentathionate have been described on p. 293. The salt dissolves in about 2 parts of water with reduction of temperature, forming a perfectly clear, transparent, and neutral solution. It is not soluble in alcohol. The aqueous solution cannot be kept long without change; after a few days, sulphur separates and potassic tetrathionate remains in solution.

The presence of a little hydric sulphate prevents this decomposition. The crystals which are obtained by evaporation from an acidulated solution are frequently crossed by fissures. The aqueous solution can be boiled for a short time without apparent change; if, however, the boiling is continued for 15 or 20 minutes, then the odour of hydric sulphide becomes perceptible. A piece of sheet copper or silver will turn black in the course of a few days in the aqueous solution in consequence of the formation of metallic sulphides. The brown colour of a solution of iodine in potassic iodide is, in the course of a day or two, decolorised by potassic pentathionate. Potassic permanganate produces a brown precipitate and hydric sulphate is formed which remains in solution. Platinum black placed in a perfectly neutral solution of potassic pentathionate causes the latter to become intensely acid, and to comport itself with baric chloride like a sulphate. Sulphur is not precipitated in this reaction. Potassic pentathionate decomposes at high temperatures as represented by the equation—

$$2K_2S_5O_6,3H_2O = 2K_2SO_4 + 2SO_2 + S_6 + 3H_2O.$$

The reactions of Wackenroder's solution have hitherto been described as the reactions of pentathionates. But Wackenroder's solution is a mixture of at least three polythionates. Being in possession of some very pure pentathionate, I, therefore, took the opportunity to study its reactions somewhat minutely.

Reactions characteristic of Pentathionates.

I. An ammoniacal solution of silver nitrate causes in a solution of potassic, ammonic, or baric pentathionates a brown coloration which

rapidly becomes darker, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetra-thionates, potassic thiosulphate, or ammonic sulphite. An ammoniacal solution of silver nitrate also seems to have no effect on them. Consequently a pentathionate, even if present in very small quantity, can be detected by means of this reaction in a mixture containing potassic tri- and tetra-thionates and sodic, potassic, or ammonic thiosulphates.

The solution of zinc in sulphurous acid produces with an ammoniacal solution of silver nitrate an immediate grey precipitate, and the supernatant liquid appears clear and colourless.

II. Potassic hydroxide, in solutions of pentathionates, immediately produces a separation of sulphur. As tri- and tetra-thionates and thiosulphates are not changed by this reagent, a proportionally small quantity of a pentathionate can be detected in a mixture of the four salts by addition of potassic hydroxide. The latter, however, is not so sensitive a reagent as the ammoniacal silver solution.

III. Ammonia added to a solution of potassic pentathionate causes, after about *one or two* minutes, a precipitation of sulphur.

IV. Sulphuretted hydrogen produces, in an ammoniacal solution of a pentathionate, an immediate precipitate of sulphur.

V. An ammoniacal solution of mercuric cyanide produces with potassic pentathionate a black precipitate, by degrees at ordinary temperatures, at once at 100° C.

VI. Ferric chloride, plumbic nitrate, cupric chloride, cupric acetate, cobaltic nitrate, zinc sulphate, cupric sulphate, plumbic acetate, hydric chloride, and baric chloride cause no change in solutions of potassic pentathionate.

General Reactions of Polythionates and Thiosulphates.

I. Mercurous nitrate produces with penta- and tetra-thionates a fine yellow, and with trithionates and thiosulphates a black precipitate.

II. Cupric sulphate mixed with solutions of potassic tri-, tetra-, or penta-thionates or an aqueous solution of sulphurous acid, or the solution of zinc in sulphurous acid, causes no apparent change at common temperatures.

The same reagent does not affect tetra- and penta-thionates at 100°, but produces at this higher temperature with trithionates or thiosulphates a black, and with the solution of zinc in sulphurous acid a red precipitate.

Cupric sulphate added to a solution of ammonic sulphite produces a yellow precipitate at common temperatures.

III. Hydric chloride does not change solutions of tetra- and penta-

thionates, but in about ten minutes in such as contain trithionates, and in about one minute in those of thiosulphates, it causes a separation of sulphur and sulphurous acid. A mixture of the four salts became turbid in two minutes.

IV. Ferric chloride causes transient coloration in the following solutions:—

a. Thiosulphates, violet changing to yellow.

b. Sulphurous acid in water, brown changing to yellow.

c. Zinc in aqueous sulphurous acid, brown changing to colourless.

The reagent causes a permanent brown colour in aqueous solution of ammonic sulphite.

V. Baric chloride produces in solutions of sodic or potassic thiosulphate a white, crystalline precipitate which, even in boiling water, is only sparingly soluble, but it does not change solutions of the polythionates at common temperatures, or those of tetra- and penta-thionates at 100°. Thiosulphates and trithionates can be detected in a mixture of the two in the following manner:—Chloride of barium is added to the neutral mixture as long as a precipitate is formed; the latter is baric thiosulphate, and can be proved to be so by means of ferric chloride and hydric chloride respectively. The filtrate from the baric thiosulphate is boiled for about five minutes, when, if barium trithionate is present, the smell of sulphurous acid will appear, and a white precipitate will be thrown down, insoluble in hydric chloride, and not volatile at a red heat on a piece of platinum-foil.

These reactions are not observed with baric dithionate.

If free acid should happen to be present in the original mixture, it must be neutralised with baric carbonate.

Zinc Pentathionate

could not be obtained in a pure state. 45 c.c. of Wackenroder's solution of the sp. gr. 1·325 were mixed with a concentrated solution of 22 grams of zinc acetate, $Zn(C_2H_3O_2)_2,3H_2O$, and the mixture allowed to evaporate at common temperatures. A crystalline mass and a very little mother-liquor remained after two days' exposure to a current of air in a draught closet. The residue (46 grams) was pressed between layers of blotting-paper, and then dissolved in 30 c.c. of water, which were acidulated with a little hydric sulphate. No insoluble matter remained behind. The solution left to spontaneous evaporation deposited nothing but crystals of zinc sulphate. The mother-liquor remained liquid in common air, but in dry air, under a bell-jar over pieces of potassic hydroxide, solidified to a white amorphous mass like porcelain, which dissolved again in very little water. The solution gave the reactions of a pentathionate.

The solid residue decomposed completely in the course of two months, sulphur, zinc sulphate, and probably sulphurous acid being the products found.

Cupric Pentathionate

was obtained in small, fine, blue crystals by the following method:—20 grams of cupric acetate were dissolved in 250 c.c. of water and the solution mixed with 45 c.c. of Wackenroder's solution of sp. gr. 1·325, and the mixture left to evaporate on two large plates in a draught closet at ordinary temperatures. After two days, a blue crystalline mass was formed on each plate, the residue of one plate was pressed between blotting-paper, and then dissolved in water acidulated with hydric sulphate. A few brown flakes remained undissolved. The blue filtrate from these during spontaneous evaporation, yielded long, fine needles in such abundance that the whole appeared like jelly, and this, when placed on bibulous paper, left a blue, solid mass which could not be dried over hydric sulphate without decomposition. It turned brown, and was, after this change of colour, only partially soluble in water. The residue on the second plate also changed its colour in the course of two days from blue to brown, because a portion of it had undergone a similar decomposition to the needle-shaped crystals mentioned above. The brown mass was pressed between layers of filtering-paper and then extracted with water. A portion dissolved, forming a blue solution and a brown solid, in appearance like cuprous oxide, was left. The blue solution which was allowed to evaporate at common temperatures yielded crystals without decomposition. Three crops of crystals were obtained; the first and second consisted of cupric sulphate, the third of fine prismatic crystals of cupric pentathionate; 0·460 gram of the latter dried over hydric sulphate and dissolved in bromine-water gave by the usual methods 0·095 gram of cupric oxide, 1·350 gram of baric sulphate, and 0·002 gram of sulphur; 100 parts contain—

	Found.	Theory. $CuS_5O_6 + 4H_2O$.
Copper	16·49	16·11
Sulphur....	40·74	40·92

Cupric pentathionate is easily soluble in water. Mercurous nitrate produces in the solution a yellow, and ammonia a blue precipitate; the latter is soluble in an excess of the reagent. The blue ammoniacal solution thus obtained reacts with ammonia-silver nitrate like potassic pentathionate. Potassic hydroxide causes in solution of cupric pentathionate a blue precipitate which is only partially soluble in hydric chloride, leaving a residue of sulphur. Similar experiments with a

mixture of potassic tetrathionate and cupric sulphate in place of cupric pentathionate, gave no brown colouring with the silver solution, and no precipitate of sulphur with potassic hydroxide.

A brown solid, a product of decomposition of one of the salts contained in the original mixture of Wackenroder's solution and cupric acetate, has been mentioned on p. 300; the mode of formation and the composition of this substance I have not accurately ascertained. Wackenroder's solution contains an acid with more sulphur than the pentathionic acid, probably hexathionic acid. The atomic ratio of copper to sulphur in the brown product was found to be = 1 : 4. From this, it would appear probable that it is formed from cupric hexathionate, according to the equation—

$$CuS_6O_6 + 2H_2O = 2H_2SO_4 + CuS_4.$$

A more detailed and accurate examination was not carried out because the substance absorbed oxygen from the air. A tube containing a portion which had been dried over hydric sulphate for the purposes of analysis, increased 0·035 gram in weight in two weeks. The brown product of decomposition resembled in colour and other properties the precipitate which forms on the addition of the higher sulphides of potassium to a solution of cupric sulphate. The colour is at first a bright red or reddish-brown, but during washing on the filter acquires a darker colour, no doubt in consequence of oxidation.

Examination of the Mother-liquor of Potassic Pentathionate.

According to the experiments described so far, Wackenroder's solution—the pentathionic acid of the text-books—is a mixture of at least two acids, tetra- and penta-thionic acids. The tetrathionic acid is not a product of decomposition of pentathionic acid, because a Wackenroder solution can be evaporated with potassic acetate with precipitation of very little sulphur. We have now to examine the mother-liquors (pp. 293, 294) from which potassic tetra- and penta-thionate had separated by crystallisation. For this purpose, the filtering-paper which had been used to free the crystals from adhering mother-liquor (p. 294) was extracted with water, and the extract mixed with the mother-liquors which had been poured off the crystals (p. 295).

The united liquids contained hydric sulphate, according to my calculation a quantity capable of decomposing 8 grams of potassic acetate. A concentrated solution of a little less than this quantity of potassic acetate was now added, and the entire mixture left to evaporate on plates in a draught closet. Nearly all the water had disappeared in two days, and a solid residue with very little mother-

liquor was left. This was pressed between layers of blotting-paper, and then dissolved in 30 c.c. of water acidulated with 1 c.c. of hydric sulphate. Only a little sulphur, according to my estimate not more than 0·01 gram, remained undissolved. The weight of the dissolved portion was 18 grams. The filtrate from the small quantity of sulphur was clear and slightly yellow. In the course of a day, however, it turned turbid and a few milligrams of sulphur separated. After a second filtration, it remained clear.

With reagents, it acted like a pentathionate, with this difference, that ammonia caused an *immediate* copious precipitate of sulphur, and a similar precipitate was obtained at 100° with cupric sulphate. The solution was put into a glass vessel with a flat bottom, and allowed to concentrate at ordinary temperatures. During the evaporation, solid matter separated and was collected in six portions.

The 1st portion consisted of potassic tetra- and penta-thionate crystals. The 2nd appeared as a crust of warty formation, in which no crystalline structure could be discovered by means of a lens. The 3rd formed small six-sided plates, the 4th was like the 2nd, and the 5th and 6th resembled the 3rd portion. The mother-liquor which remained at last was so small in volume that no further experiments could be made with it.

The 2nd and the 4th portions appeared to be formed of the same substance, and were homogeneous throughout. They were therefore united, washed with dilute alcohol, and dried over hydric sulphate. This substance appeared to be potassic hexathionate, mixed with some potassic hydric sulphate and free sulphur. I could not remove these impurities. If the substance is dissolved in water with a little hydric sulphate and left to evaporate, it will, although sulphuric acid is present, partially decompose with separation of sulphur and production of pentathionate. I attempted, therefore, to determine the impurities and calculate the composition of the remainder. The substance is well characterised by its physical and chemical properties. I will, on the basis of the following determinations, call it potassic hexathionate.

I. 0·240 gram was dissolved in water slightly acidulated with hydric chloride and precipitated with baric chloride. The precipitate contained, besides baric sulphate, also the free sulphur which was mechanically mixed with the potassic hexathionate. The precipitate was collected on a weighed filter and dried over hydric sulphate. Its weight was found to be 0·033 gram. At a red heat, the weight diminished to 0·024 gram. The difference of the two weights, 0·009 gram, represents the weight of the free sulphur.

II. 0·288 gram oxidised with bromine-water, and the products precipitated with baric chloride, gave 1·046 gram of baric sulphate,

and 0·3124 gram gave after heating to redness 0·1385 gram potassic sulphate. 0·330 gram of the substance burnt with potassic chromate gave 0·021 gram water.

According to the data given under II, 100 parts of the substance contain—

Potassium	19·92
Sulphur	49·89
Oxygen	23·83
Water	6·36
	100·00

According to the determinations of I, 3·75 per cent. of sulphur are present in the free state, and 1·37 per cent. in the form of potassic hydric sulphate. 5·12 per cent. of sulphur have, consequently, to be deducted from 49·89 per cent. as found under II. If likewise the potassium, oxygen, and hydrogen of the potassic hydric sulphate are subtracted, the following quantities are left:—

Potassium	18·25
Sulphur	44·77
Oxygen	21·09
Water	5·98
	90·09

And in 100 parts:—

	Found.	Theory. $K_2S_6O_6 + 1{\cdot}5H_2O$.
Potassium	20·25	19·84
Sulphur	49·69	48·85
Oxygen	23·40	24·42
Water	6·63	6·87
	99·97	99·98

The atomic proportions are—

$$K_2S_{5\cdot96}O_{5\cdot85} + 1{\cdot}41H_2O.$$

Sulphur and potassium have been found too high, and, accordingly oxygen somewhat too low.

Potassic hexathionate separates from its solution in crusts of warty masses without crystalline structure. More pure than the sample analysed, I found some amongst the 5th crop of crystals (p. 302). As this did not contain free sulphur, it dissolved in water to a clear solution.

The aqueous solutions of this salt decompose with separation of sulphur, even when free hydric sulphate is present, and are thus

distinguished from those of the pentathionate. Potassic nitrate, which completely precipitates δ-sulphur (sulphur in the colloïdal condition in solution) does not change the solution of the hexathionate. Ammonia produces a precipitate of sulphur immediately (difference from pentathionate), and ammoniacal solution of silver nitrate, potassic hydroxide, and mercurous nitrate, react with hexathionate as with pentathionate.

The crystals obtained from the mother-liquors of potassic hexathionate (p. 302) were potassic pentathionate rendered impure by potassic sulphate. 0·369 gram gave after ignition 0·183 gram of potassic sulphate.

In 100 parts:—

	Found.	Theory.
Potassium..	22·23	21·60

The impure substance, which has been described as potassic hexathionate, decomposes so very easily that I could not hope to prepare it in a perfectly pure state. I have therefore, by the following experiments, attempted to prove the existence of polythionates containing more sulphur than pentathionates, and thus increase the probability of the existence of hexathionates.

The Wackenroder's solution used in these experiments was not prepared exactly as described on p. 281. Sulphuretted hydrogen was passed into *smaller* quantities of sulphurous acid than in former preparations. Not more than 120 c.c. were taken for each experiment, with the result that the decomposition of the sulphurous acid required less time than before. Hydric sulphide was passed for one hour through the sulphurous acid solution, and again on the next day for two hours. The reactions were then completed, and no more free sulphurous acid could be observed. The resulting solution was now concentrated on the water-bath until it showed the sp. gr. 1·257, and then filtered from the precipitated sulphur.

Reactions of the Concentrated Solution.

It produced with potassic hydroxide, ammoniacal silver nitrate, mercurous nitrate, and cupric sulphate respectively, the reactions of potassic pentathionate. Ammonia gave a copious precipitate of sulphur. No difference in this respect could be observed when the reagent was added in large excess. Samples of Wackenroder's solution, prepared as described on p. 281, did not show this behaviour.

Analysis of the Concentrated Solution.

10 c.c. of the sp. gr. 1·257 were diluted with 15 c.c. of water.

I. 5 c.c. of the diluted liquid were precipitated with baric chloride. Weight of precipitate = 0·121 gram. Free sulphur was not present.

II. 5 c.c. of the diluted liquid when boiled with mercuric cyanide, gave 0·969 gram of a black precipitate, consisting of mercury and sulphur, which was collected on a previously weighed filter. The filtrate from this precipitate gave with baric chloride 1·692 gram of baric sulphate. 0·907 gram of the mercuric cyanide precipitate dissolved in bromine-water gave 0·136 gram of sulphur and 1·052 gram of baric sulphate, from which data we calculate for the entire precipitate of 0·969 gram, 0·299 gram of sulphur, and by difference 0·670 gram of mercury.

III. 5 c.c. of the diluted liquid, boiled with mercuric cyanide, gave 0·971 gram of a precipitate consisting of mercuric sulphide and sulphur. The filtrate mixed with baric chloride yielded 1·682 gram of baric sulphate.

IV. 5 c.c. of the diluted liquid oxidised with bromine-water, and precipitated with baric chloride, gave 3·686 grams of baric sulphate and 0·018 gram of sulphur. According to determinations I, II, and III, 5 c.c. of the diluted liquid contain 0·5135 gram of sulphur in combination in the form of polythionic acids. According to determinations I and IV, 5 c.c. contain, after deduction of the sulphur present in the form of sulphuric acid, 0·507 gram of sulphur.

The two numbers 0·513 and 0·507 are sufficiently near to allow the conclusion that the liquid under examination contains besides some sulphuric acid, only sulphur compounds of the form $H_2S_xO_6$ (polythionic acids).

The atomic ratio of the sulphuric acid, formed by boiling the diluted liquid with mercuric cyanide, to the mercury and sulphur of the precipitate formed in the same operation, is—

[I and II] $SO_3 : Hg : S = 2 : 1 : 2{\cdot}78$
[I and III] $SO_3 : Hg : S = 2 : 1 : 2{\cdot}79$

which means that the average composition of the polythionic acids of the solution is nearly expressed by the formula $S_{4\cdot8}O_5$ or $H_2S_{4\cdot8}O_6$, a formula which would correspond to 4 mols. of hydric pentathionate and 1 mol. of hydric tetrathionate (see p. 287): viz., a Wackenroder solution containing 4 mols. of pentathionic acid and 1 mol. tetrathionic acid would give the analytical results described.

From the above determinations, we calculate that 1 c.c. of Wackenroder's solution of sp. gr. 1·257 contains 0·389 gram of acid of the average composition $S_{4\cdot75}O_5$, and 0·0207 gram sulphuric acid (SO_3). 0·389 gram of acid, $S_{4\cdot75}O_5$, can decompose 0·3285 gram of potassic acetate, $KC_2H_3O_2$, and produce 0·5463 gram anhydrous polythionate. 95 c.c. of Wackenroder's solution of the sp. gr. 1·257 were, therefore,

mixed with a solution of 30 grams of potassic acetate and left to concentrate at ordinary temperatures. The crystalline residue remaining after 24 hours' evaporation weighed, after pressing between filtering-paper, 45 grams. According to theory, 30 grams of potassic acetate can produce 49·8 of anhydrous polythionates of the average composition $K_2S_{4\cdot75}O_6$. The mother-liquor of the crystalline residue which had been absorbed by the Swedish filtering-paper was extracted with water and the aqueous extract examined separately. The pressed residue, 45 grams, was dissolved in 80 c.c. of water containing 1 c.c. hydric sulphate at 50°, a few milligrams of sulphur were separated by filtration, and the clear filtrate left to crystallise at common temperatures in a vessel with a flat bottom. A crop of fine crystals, consisting partly of potassic tetrathionate and partly of potassic pentathionate, formed in the course of a few days. The two descriptions of crystals were easily separated from each other. 24·5 grams of potassic tetrathionate and 10·5 grams of potassic pentathionate were collected.

The degree of purity of the crystals can be judged by the following determinations :—

a. Potassic pentathionate.

0·407 gram gave 0·200 gram of potassic sulphate, therefore, 100 parts contain 22·02 parts of potassium. Theory requires 21·6 parts.

b. Potassic tetrathionate.

0·544 gram gave 0·308 gram of potassic sulphate; 100 parts contain, therefore, 25·38 parts of potassium instead of 25·82 parts as required by theory. The potassic pentathionate contains 0·42 per cent. of potassium more, and the potassic tetrathionate, 0·44 per cent. potassium less than the theoretical quantities, which means, that the picked out pentathionate contained 10 per cent. of tetrathionate, and the selected tetrathionate 10 per cent. of pentathionate. Several of the smaller crystals of both salts frequently grow together.

95 c.c. of Wackenroder's solution of 1·257 sp. gr. contain according to analysis 36·96 grams of acids of the average composition $S_{4\cdot75}O_5$. If the solution contains for every molecule of tetrathionic acid 3 mols. of pentathionic acid, then after addition of 30 grams of potassic acetate it should have produced 41·4 grams of hydrated potassic pentathionate and 11·5 grams of potassic tetrathionate. Instead of these quantities, only $\frac{1}{4}$ of the theoretical amount of pentathionate and more than double the theoretical quantity of tetrathionate were actually obtained.

The assumption that Wackenroder's solution contains only tetrathionic and pentathionic acids is therefore incorrect; it must contain besides these another acid with more sulphur than pentathionic acid.

95 c.c. of Wackenroder's solution of 1·257 sp. gr. contain according

to analysis 24·27 grams of sulphur and 12·73 grams of oxygen united to polythionic acids.

10·5 grams potassic pentathionate ($2K_2S_5O_6,3H_2O$), collected as described, contain 4·66 grams of sulphur and 2·33 grams of oxygen united as S_5O_5.

24·5 grams of potassic tetrathionate ($K_2S_4O_6$) contain 10·38 grams of sulphur and 6·49 grams of oxygen united as S_4O_5.

Now if we subtract the sulphur and oxygen of the tetrathionic (S_4O_5), and the pentathionic acids (S_5O_5), contained in the potassium salts, from the sulphur and oxygen of the polythionic acids contained in the 95 c.c. of Wackenroder's solution, the remainder will be the sulphur and oxygen of the acids contained as potassic polythionates in the united mother-liquors.

$$24{\cdot}27 \text{ grams S} - (4{\cdot}66 + 10{\cdot}38)\text{S} = 9{\cdot}24 \text{ grams S.}$$
$$12{\cdot}73 \text{ grams O} - (2{\cdot}33 + 6{\cdot}49)\text{O} = 3{\cdot}91 \text{ grams O.}$$

Now, $9{\cdot}24 : 3{\cdot}91 = 189 : 80 = S_{5\cdot9} : O_5$, for which we may take—

$$S_6O_5.$$

That is to say, the average composition of the potassic polythionates contained in the mother-liquors of the above potassic penta- and tetra-thionates is represented by the formula—

$$K_2S_6O_6,$$

or corresponds to the composition of a hexathionate.

The united mother-liquors and aqueous extracts of the Swedish filtering-paper were mixed with 3 grams of potassic acetate in order to convert the greater portion of hydric sulphate present into potassic sulphate, and then placed on a plate in the window of a draught closet. The evaporation was finished in 24 hours. The solid residue which was still moist, was pressed between layers of filtering-paper, and in this condition weighed 11·5 grams. It was now put in 10 c.c. of water, which contained $\frac{1}{4}$ c.c. of hydric sulphate; it all dissolved except a trace of sulphur, which was separated by means of a filter. The filtrate, which, however, did not appear to be quite clear, was allowed to concentrate at common temperatures. After a few days, a crust of warty formations appeared without crystalline structure. This was removed, and the mother-liquor a second time gave a crust of warty matter, which, like the first, was dried on blotting-paper. The remaining mother-liquor was now practically exhausted. A few days after their preparation, the two separations of warty formations began to decompose with development of sulphurous acid. In order to prevent this decomposition, they were placed in water. The first dissolved with the exception of some sulphur, the second left a proportionately small quantity of a sparingly soluble potassium salt.

The molecules of potassic hexathionate are evidently of a most unstable nature, and little hope was left of their complete separation from other matter.

The two aqueous solutions mentioned just before were united, filtered, and the atomic ratio of potassium, sulphur, and oxygen of the salt or salts in solution determined according to Kessler's method.

I. Determination of sulphates.

5 c.c. were mixed with baric chloride and 0·33 gram of baric sulphate obtained.

II. Determination of sulphur, oxygen, and metal in the polythionates.

5 c.c. of the filtrate were boiled with a solution of mercuric cyanide. The precipitate consisting of sulphur and mercury, weighed 0·333 gram, and the filtrate from this precipitate gave with baric chloride 0·831 gram of baric sulphate. After deducting the sulphate found under I, a residue of 0·501 gram is left, which contained 0·0688 gram of sulphur.

III. Determination of the mercury and sulphur in the precipitate mentioned under II.

0·313 gram of the precipitate were digested with bromine-water until all the mercury was dissolved. 0·028 gram of sulphur was left undissolved, and the filtrate from this sulphur gave with baric chloride 0·635 gram of baric sulphate, which contains 0·0872 gram of sulphur.

The filtrate from the baric sulphate gave with hydric sulphide 0·228 gram of mercuric sulphide, which contains 0·196 gram mercury. If, however, the mercury is taken to be equal to the difference between the weight of substance taken and the sulphur found, then its quantity would be = 0·1978 gram. The last number I consider to be more correct than the former, and, therefore, I shall adopt it.

From these numbers we obtain for the composition of 0·333 gram of precipitate found in II, 0·122 gram of sulphur and 0·211 gram of mercury. The atomic ratio of the sulphur in the sulphuric acid produced by boiling with mercuric cyanide to the mercury and sulphur of the precipitate formed at the same time, is therefore—

$$S \text{ of } SO_3 : Hg : S = 2{\cdot}04 : 1 : 3{\cdot}62.$$

If the sulphuric acid of 0·501 gram of baric sulphate found in II is added to the mercury and sulphur of the mercuric cyanide precipitate, we obtain the weight of the mercuric polythionate, and if we replace in this the mercury by its equivalent of potassium, we have the average composition of the potassic polythionates of the solution, as expressed by the formula—

$$K_2S_{5\cdot61}O_{6\cdot11}.$$

Therefore, the solution contains a polythionate with more sulphur than the pentathionate.

The following experiment shows that besides sulphates and polythionates, no other sulphur compounds are present in the solutions.

IV. 5 c.c. treated with bromine-water until all the sulphur was oxidised to sulphuric acid and precipitated with baric chloride, gave 1·728 gram of baric sulphate. Deducting from this weight the amount of sulphate found in I, there remains a quantity of baric sulphate which contains 0·192 gram of sulphur.

According to I, II, and III, the total sulphur present in 5 c.c. of the liquid as polythionates is = 0·191 gram. Hence it follows that the solution contains only sulphates and polythionates.

Reactions of the Solution.

Although clear immediately after filtration, the liquid soon became turbid, and deposited a comparatively small precipitate of sulphur. This precipitate did not further increase, even in the course of weeks. But as soon as it was separated by filtration, the clear liquid in the course of an hour again became turbid and soon formed a quantity of precipitate about equal to the former. Then the precipitation would stop until the liquid was filtered, when it would commence again. I have repeated the filtration five or six times always with the same result. These observations I explain as follows:—The liquid contains easily decomposable potassic hexathionate, which decomposes with separation of sulphur, but the latter separates in a condition in which it can recombine with potassic pentathionate and produce a higher polythionate. In every unit of time, a certain portion of sulphur is set free and a certain portion redissolved.

The precipitation stops when both actions become equal. Hydric chloride, ferric chloride, cobalt sulphate, and cupric sulphate caused no change in the liquid. Ammonia gave a copious precipitate consisting of yellow flakes of sulphur; and a large excess of ammonia, a white crystalline precipitate soluble in an excess of water.

Potassic hydroxide, ammoniacal solution of silver nitrate, mercurous nitrate, and hydric sulphide, respectively, gave the same reactions as with a pentathionate.

The experiments described prove that Wackenroder's solution contains in addition to tetra- and penta-thionic acid, one or more acids of similar constitution, but richer in sulphur than the two acids named. The acid is probably hexathionic acid.

If during the preparation *insufficient* hydric sulphide has been passed through the sulphurous acid, trithionic acid also will be present. The small amount of hydric sulphate which I found in

Wackenroder's solution is most probably the result of the oxidising action of the air on sulphurous acid.

Lenoir, Ludwig, Kessler and others have attempted the preparation of pentathionates by the complete or partial neutralisation of the acids in Wackenroder's solution and precipitation of the salts formed by means of alcohol. The results were, as might be expected, very discordant. For it is clear that the concentration of Wackenroder's solution, as well as the strength and volume of the alcohol used, must have, according to the experiments described in this paper, an influence on the composition of the precipitate.

Kessler obtained potassic tetrathionate and sulphur, Ludwig a mixture of baric tetra- and penta-thionates, and Lenoir a precipitate nearly of the composition of baric pentathionate.

Some experiments of my own show the variations in the composition of the precipitates very clearly. Wackenroder's solution of sp. gr. 1·25 was neutralised with baric carbonate, filtered, and then precipitated with twice its volume of alcohol. The crystalline precipitate was redissolved in a small quantity of water, the solution separated by filtration from a little sulphur, and then reprecipitated by alcohol. The precipitate obtained in this way had nearly the composition of baric pentathionate, but might be a mixture of baric tetra-, penta-, and hexa-thionates.

On addition of more alcohol to the first filtrate from this precipitate, it gave another precipitate in which barium and sulphur were contained in the atomic proportion

$$Ba : S = 1 : 4{\cdot}28.$$

The filtrate from the last precipitate gave with more alcohol a third precipitate of the atomic ratio

$$Ba : S = 1 : 3{\cdot}8,$$

and if the alcohol which was added in three portions had been added at once, the ratio of barium to sulphur in the precipitate would probably have been $= 1 : 4{\cdot}6$. It is clear that by such methods pure substances cannot be obtained with certainty.

The Wackenroder's solution has been proved in this paper to contain before its evaporation large quantities of sulphur in a new modification, δ-sulphur in solution, and besides this tetra-, penta-, and probably hexa-thionic acids.

We have now to explain the formation of these products from the original materials—sulphuretted hydrogen, sulphurous acid, and water. This problem is one of the most complicated in chemistry.

B. On the Formation of the Constituents of Wackenroder's Solution.

Decomposition of an Aqueous Solution of Potassic Pentathionate.

A concentrated solution of this salt was allowed to stand for a few months in a beaker covered with a piece of filtering-paper. From time to time, some water was added in order to make good the loss caused by evaporation. Very soon, in less than 48 hours after the preparation of the solution, sulphur began to separate, and slowly continued to do so for several weeks, but even after three months the decomposition was not quite complete, for potassic pentathionate could still be detected (see p. 298). As soon as the separation of sulphur appeared to be practically complete, the solution was passed through a filter and allowed to evaporate spontaneously. A fine crop of crystals of potassic tetrathionate was obtained.

1·228 gram dried over hydric sulphate gave after ignition 0·7035 gram of potassic sulphate. 1·0695 gram of the same substance oxidised with bromine-water gave 0·090 gram of sulphur, and 2·616 grams of baric sulphate, from which data we calculate for 100 parts—

	Found.	Theory. $K_2S_4O_6$.
Potassium ..	25·68	25·82
Sulphur	42·02	42·38

The decomposition can be represented by the equation—

$$K_2S_5O_6 = K_2S_4O_6 + S.$$

The mother-liquor contained, however, small quantities of potassic tri- and penta-thionates and some potassic and hydric sulphates. The sulphur on the filter could not be washed because it passed through the pores of the filter with the water. The crystals of potassic tetrathionate obtained formed with water a neutral solution which was not changed on addition of potassic hydroxide, or of an ammoniacal solution of silver nitrate.

Decomposition of an Aqueous Solution of Potassic Tetrathionate.

Fine large crystals of the salt were carefully examined.

1·14 gram dried over hydric sulphate left after ignition 0·656 gram of potassic sulphate. 0·6945 gram of the same substance oxidised with bromine-water and the solution precipitated with baric chloride gave 2·145 grams of baric sulphate. Hence in 100 parts—

	Found.	$K_2S_4O_6$.
Potassium ..	25·79	25·82
Sulphur....	42·41	42·38

The aqueous solution of this substance was not changed on addition of ammonia-silver nitrate and potassic hydroxide respectively. Also cupric sulphate produced no reaction with it at 100°. The substance, therefore, is pure potassic tetrathionate.

0·5 gram of this pure salt was dissolved in 10 c.c. of water. The neutral solution was left standing for 12 days at 18°. It was now strongly acid but still clear, and smelt strongly of sulphurous acid. The appearance of sulphurous acid without separation of sulphur indicated the probable formation of a compound richer in sulphur than the tetrathionate.

I now prepared another solution of 0·5 gram of potassic tetrathionate in 10 c.c. of water, and made with this, and with the solution 12 days old, the following comparative experiments:—

Reagents.	New solution of potassic tetrathionate.	Twelve-days old solution of potassic tetrathionate.
Litmus	neutral	Strongly acid.
$BaCl_2 + HCl + H_2O$.	no change	Copious precipitate.
$AgNO_3 + NH_4HO$.	„	Brown colouring & black precipitate.
NaHO	„	Precipitation of much sulphur.
$CuSO_4$	no change at 100°	Black precipitate at 100°.
NH_4HO	no change	Turbid after a few minutes.
$Hg_2(NO_3)_2$	yellow precipitate	Grey precipitate.
Fe_2Cl_6	no change	No change.

These reactions prove that an aqueous solution of potassic tetrathionate at 18° slowly decomposes into potassic pentathionate and potassic trithionate, sulphurous acid, and potassic sulphate, as represented by the following equations:—

$$2K_2S_4O_6 = K_2S_3O_6 + K_2S_5O_6.$$

Further on it will be shown that potassic trithionate decomposes as follows:—

$$3K_2S_3O_6 = 2K_2SO_4 + 2SO_2 + K_2S_5O_6,$$

and the spontaneous decomposition of potassic tetrathionate at 18° is fully explained.

The following experiment will furnish an idea of the rate at which the decomposition proceeds:—

The temperature of my laboratory is from October to May nearly

constant, 18°, so that all these experiments have been performed practically at the same temperature.

A solution of 1 gram of potassic tetrathionate in 10 c.c. of water was tested at intervals as described in this table.

Time in hours after preparation.	Reagents.	
	Litmus.	Ammonia-silver nitrate.
22	neutral	No change.
76	"	Feeble reaction of pentathionate.
96	"	Reaction of pentathionate.
168	slightly acid	Strong reaction of pentathionate.
288	strongly acid	Very strong reaction of pentathionate.

Ammonia-silver nitrate is the most sensitive reagent for pentathionates. The formation of pentathionate could only be detected with sodic hydroxide after the solution had been standing more than 168 hours.

The crystals of potassic tetrathionate kept in a closed bottle smelt of sulphurous acid after some time. Water enclosed in cracks and fissures of the crystals is the cause of this decomposition. The perfectly dry salt can be kept without the slightest change.

Decomposition of an Aqueous Solution of Potassic Trithionate.

The equation on p. 312, representing the decomposition of this salt in aqueous solutions, has to be proved. The salt used in the following experiments had been prepared by the action of sulphurous acid on potassic thiosulphate, and two or three times recrystallised from hot water.

1·2855 gram dried over hydric sulphate gave after ignition 0·8275 gram potassic sulphate.

0·643 gram of the same substance oxidised with bromine-water gave 1·662 gram of baric sulphate.

Hence in 100 parts—

	Found.	$K_2S_3O_6$.
Potassium..	28·85	28·88
Sulphur....	35·49	35·55

A clear, neutral solution of 1 gram of this salt in 10 c.c. of water, soon after its preparation gave no reaction with ammonia-silver nitrate

or potassic hydroxide, and therefore did not contain any pentathionate; after standing 24 hours, the solution had acquired an acid reaction *without separation of sulphur.*

The decomposition can be represented by the equation—

$$2K_2S_3O_6 = K_2S_4O_6 + K_2SO_4 + SO_2.$$

Potassic pentathionate was not detected at this stage of the transformation. Six days after the preparation of the solution, potassic sulphate and sulphurous acid were found in abundance, and comparatively large quantities of potassic pentathionate were detected by means of ammonia-silver nitrate and potassic hydroxide respectively.

It follows, therefore, that an aqueous solution of potassic trithionate decomposes at 18° slowly into potassic sulphate, sulphurous acid, and sulphur, but the latter is not set free, as it enters into combination with potassic trithionate, forming tetra- and penta-thionate respectively—

$$3K_2S_3O_6 = 2K_2SO_4 + 2SO_2 + K_2S_5O_6.$$

A solution of one of the three salts, potassic penta-, tetra-, or trithionate, will contain, if left to itself for some time, all three salts. An attempt to separate the salts so formed by crystallisation failed, because the quantity of material (6 grams) I used was not large enough for the purpose, the crystals being too small and interlaced to allow of their mechanical separation.

The question, "Can common sulphur combine with potassic tri- or potassic tetra-thionate, as sulphur does *statu nascendi?*" suggested the following experiment:—

0·940 gram of sulphur which had been crystallised from carbonic disulphide was left in contact with a concentrated solution of potassic tetrathionate for 24 hours. The sulphur was, after the lapse of this time, collected on a weighed filter, and found to have lost only 1 mgrm. in weight, and the solution of the potassic tetrathionate appeared to be quite unaltered; no trace of pentathionate could be detected in it.

From this experiment, and from a similar one made by Mr. Lewes with sulphur and hydric tetrathionate, rhombic sulphur appears to be insoluble in potassic tetrathionate.

Spring asserts, however, that hydric tetrathionate dissolves flowers of sulphur if digested with it for a month or two (*Annalen*, **213**, 339). He analysed the solutions according to Kessler's method, by boiling with mercuric cyanide, and found that the ratio of sulphur in the mercuric sulphide to the sulphur precipitated in the free state increased during the digestion of hydric tetrathionate with sulphur.

Hydric tetrathionate gave with mercuric cyanide (p. 287)—

$$[H_2SO_4] : HgS : S = 1{\cdot}98 : 1 : 1{\cdot}04.$$

And after treatment with flowers of sulphur—

$$H_2SO_4 : HgS : S \quad = - : 1 : 1{\cdot}85.$$

The change of the ratio 1 : 1·04 into 1 : 1·85 proves, according to Spring, solution of sulphur in the acid. Now there is good reason for assuming that hydric tetrathionate comports itself in an aqueous solution like the potassium salt, viz., it will decompose into hydric trithionate and hydric pentathionate, and the former changes into hydric sulphate, sulphurous acid, and sulphur, which in *statu nascendi* would recombine with undecomposed hydric tetrathionate and produce pentathionate. But if these reactions occur, then the above ratio 1 : 1·04 can change into 1 : 1·85 without the solution of an atom of sulphur in hydric tetrathionate. Therefore Spring has not proved the solubility of flowers of sulphur in hydric tetrathionate.

Potassic tetrathionate does not only combine with sulphur in *statu nascendi* set free by its own spontaneous decomposition, but generally with sulphur in *statu nascendi*, forming potassic pentathionate. Bromine-water decomposes potassic tetrathionate according to the equation—

$$K_2S_4O_6 + 2H_2O + Br_2 = 2KBr + 2H_2SO_4 + S_2.$$

If the bromine-water is added cautiously and slowly, the sulphur, instead of falling down, will combine with another portion of potassic tetrathionate and produce potassic pentathionate. Or if a solution of potassic tetrathionate is mixed with hydric sulphate, and hydric sulphide passed in excess, the following decomposition will take place :—

$$K_2S_4O_6 + H_2SO_4 + 5H_2S = K_2SO_4 + 6H_2O + 9S.$$

Also in this case the sulphur, instead of becoming free, will combine with undecomposed potassic tetrathionate and produce the pentathionate. This behaviour of sulphur in *statu nascendi* enables us to prepare potassic pentathionate from tetrathionate.

Preparation of Potassic Pentathionate from Potassic Tetrathionate.

72 grams of pure potassic tetrathionate were dissolved in 240 c.c. of water acidulated with 4 grams of hydric sulphate. A sample of this solution gave with ammonia-silver nitrate and potassic hydroxide respectively no reactions of pentathionate. A slow current of hydric sulphide was passed for one hour through the solu-

tion, and the liquid after this treatment allowed to stand for two days in a closed cylinder. The smell of sulphuretted hydrogen was gone at the end of this time without separation of much sulphur. The quantity of sulphur which had precipitated was in fact not more than would have separated if sulphuretted hydrogen water had been left standing in a closed bottle for two days. The solution now comported itself with ammonia-silver nitrate and potassic hydroxide, respectively, like one of potassic pentathionate. In order to extract this salt, the small precipitate of sulphur was separated by filtration, the clear filtrate allowed to evaporate spontaneously at common temperatures, and the crystals which formed were from time to time removed from the liquid. Seven portions of crystals were collected. The first consisted of pure potassic tetrathionate, the second contained in addition a little potassic pentathionate, the third a little more of this salt, and the last four crops of crystals were very rich in pentathionate.

These, which weighed 24 grams, were united and dissolved in 70 grams of water acidulated with 1 c.c. of hydric sulphate. The solution, left to spontaneous evaporation, gave first only crystals of potassic tetrathionate, and towards the end of the crystallisation only crystals of potassic pentathionate. The crystals were very fine, most of them a quarter of an inch in diameter, and could easily be picked out from a crystal or two of tetrathionate. A little more than 3 grams of pure potassic pentathionate was collected.

I. 0·354 gram gave after ignition 0·171 gram of potassic sulphate.

II. 0·59 gram gave 0·2855 gram potassic sulphate.
0·3845 gram completely oxidised with bromine-water gave on addition of baric chloride 1·241 gram of baric sulphate.

III. 0·19 gram of another preparation gave 0·092 gram of potassic sulphate.

In 100 parts—

	I.	II.	III.	$2K_2S_5O_6 + 3H_2O$.
Potassium	21·64	21·69	21·68	21·60
Sulphur	—	44·32	—	44·32

Action of some Acids on the Solutions of Potassic Polythionates.

Two test-tubes, one containing 10 c.c. of a pure concentrated solution of potassic pentathionate, and the other 10 c.c. of a similar solution mixed with $\frac{1}{10}$ c.c. of hydric sulphate, were corked and kept for several days near each other. The solution containing potassic pentathionate only was after eleven days quite turbid from free

sulphur, and after three weeks contained a comparatively large precipitate of sulphur. The solution, which contained besides potassic pentathionate a little hydric sulphate, appeared to be quite unchanged after three months.

Into four test-tubes, 10 c.c. of different solutions were introduced, in the 1st was a 10 per cent. solution of pure potassic pentathionate, in the 2nd a similar solution with one drop of strong hydric chloride, in the 3rd a similar solution with three drops of hydric chloride, and in the 4th a similar solution with some acetic acid. The solution of pure potassic pentathionate commenced to deposit sulphur within three days after its preparation, the one which contained hydric acetate in addition to the potassium salt, remained unchanged for a fortnight, and then entered into slow decomposition with precipitation of sulphur. The sulphur precipitate continued to increase for some weeks. After seven months, the solutions were filtered and carefully examined.

The same substances, potassic pentathionate, potassic trithionate, and potassic sulphate were found in both. The tubes which contained hydric chloride besides potassic pentathionate showed no signs of decomposition after seven months' keeping. Therefore comparatively small quantities of hydric chloride or hydric sulphate prevent the decomposition of potassic pentathionate in an aqueous solution, whilst hydric acetate exerts a retarding influence only.

The spontaneous decomposition of potassic tetrathionate is likewise prevented by the presence of about 2 per cent. of hydric sulphate; a solution of potassic trithionate acidulated with hydric sulphate decomposes apparently quite as easily as a solution of the pure salt.

6·5 grams of potassic trithionate were dissolved in 30 c.c. of water containing $\frac{1}{6}$ c.c. of hydric sulphate. After 24 hours, large quantities of sulphurous acid were observed, and in the course of two weeks precipitation of sulphur had taken place.

Spontaneous Decomposition of Wackenroder's Solution.

As this solution is a mixture of the hydrogen salts of the polythionic acids, its spontaneous decomposition might be expected if no hydric sulphate were present.

But as my solutions usually contained about 2 per cent. of this substance, the question arose whether this amount of sulphate exerts a protecting influence over the polythionates of the solution.

A sample of concentrated Wackenroder's solution could be kept for three months in a dark place without the slightest decomposition. But after this time, a slow decomposition set in, which manifested

itself by the development of sulphurous acid and the precipitation of sulphur. After two years, the liquid appeared like a strong solution of sulphurous acid and contained a proportionately large precipitate of monoclinic sulphur. The liquid above this sulphur was perfectly clear, it was separated by filtration from the sediment and then placed over pieces of potassic hydroxide under a bell-jar. After eight days, all the sulphurous acid had left the solution and combined with the potassic hydroxide. The small quantity of sulphur which had separated during the evaporation of the sulphurous acid was removed from the liquid by filtration.

The qualitative examination of the filtrate revealed the presence of a small amount of hydric trithionate, some hydric hexathionate (ammonia gave an immediate precipitate even when used in excess), and much hydric pentathionate.

The remainder of the filtrate was evaporated until its sp. gr. was 1·284. During evaporation, some sulphur separated. The filtrate from this sulphur measured 35 c.c., and was at first clear but soon became turbid. A concentrated solution of 13·5 grams of potassic acetate was added to it and the mixture placed in a draught closet. The crystalline cake, left after evaporation of the water and hydric acetate, was recrystallised from water acidulated with a little hydric sulphate. Four portions of crystals were separated and collected.

a. Crystals like potassic pentathionate.

0·510 gram gave after ignition 0·2496 gram of potassic sulphate.

In 100 parts—

	Found.	Theory.
Potassium ..	21·93	21·60

The solution of these crystals comported itself with potassic hydroxide, ammonia-silver nitrate, and mercurous nitrate respectively, like a pentathionate.

b. Crystals like potassic tetrathionate.

0·613 gram gave 0·347 gram of potassic sulphate.

In 100 parts—

	Found.	Theory.
Potassium ..	25·37	25·82

A solution of these crystals behaved with solution of potassic hydroxide, ammonia-silver nitrate, mercurous nitrate, and cupric sulphate like a tetrathionate.

c. Crystals of potassic sulphate.

d. „ „

From these experiments, it follows that Wackenroder's solution

decomposes spontaneously like the potassium salts of the polythionic acids, and that this decomposition is very slow, being incomplete even after two years, and is probably retarded but not prevented by the presence of about 2 per cent. of hydric sulphate. Such an amount of sulphate would prevent the decomposition of potassic pentathionate and tetrathionate.

Does the Air promote the Spontaneous Decomposition of Potassic Tetrathionate?

Three tubes were about half filled with a solution of 8 parts of water and 1 part of potassic tetrathionate.

Two of the tubes were exhausted by means of the air-pump and then sealed in a blowpipe flame. The third tube was closed by a cork and placed by the side of the two others. The liquids in all these tubes had become acid after 12 days, but only those in the exhausted tubes had deposited sulphur. Potassic pentathionate could be detected in all three tubes. Therefore, the decomposition of potassic tetrathionate solution had been more rapid in the exhausted tubes.

Discussion of the behaviour of the Potassic Polythionates in Aqueous Solution.

It has been shown (pp. 311 and 312) that these salts decompose in aqueous solutions according to the equations—

(1.) $K_2S_5O_6 = K_2S_4O_6 + S.$
(2.) $2K_2S_4O_6 = K_2S_5O_6 + K_2S_3O_6.$
(3.) $K_2S_3O_6 = K_2SO_4 + SO_2 + S.$

But the sulphur of this last reaction is not set free, but combines with undecomposed potassic trithionate, forming potassic tetrathionate—

$$K_2S_3O_6 + S = K_2S_4O_6;$$

or pentathionate—

$$K_2S_3O_6 + S_2 = K_2S_5O_6.$$

The last three equations can be united—

$$5K_2S_3O_6 = K_2S_5O_6 + K_2S_4O_6 + 3K_2SO_4 + 3SO_2 \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

The reactions are consequently of a reciprocal nature, that is to say, they are reversible and can take place in opposite directions apparently with equal facility. This interesting behaviour is, no doubt, in great measure dependent on the heat of formation of the polythionates.

Thomsen (*Thermochemische Untersuchungen*, **2**, 264; **3**, 236) calculates the following values for the heat of formation of the bodies in question:—

				Diff.
Hydric	dithionate.....	S_2,O_5,Aq	211080	9320
„	trithionate	S_3,O_5,Aq	201760	9330
„	tetrathionate.....	S_4,O_5,Aq	192430	9320
„	pentathionate	S_5,O_5,Aq	183110	
Potassic	dithionate.....	S_2,O_6,Aq,K_2	415720	9870
„	trithionate	S_3,O_6,Aq,K_2	405850	8640
„	tetrathionate	S_4,O_6,Aq,K_2	397210	
„	pentathionate	S_5,O_6,Aq,K_2	—	

From these numbers, it appears that the hydrogen and potassium salts of the polythionic acids develop by their formation from water and the elements, less and less heat as they become richer in sulphur. When potassic trithionate unites with 1 atom of sulphur, no less than 8640 cal. are rendered latent, and the same quantity of energy seems to be stored up when potassic tetrathionate unites with 1 atom of sulphur forming pentathionate. The compounds with regard to these sulphur atoms are endothermic. A sulphur-atom which detaches itself from a molecule of potassic tetrathionate carries away with it an amount of energy corresponding to about 9000 cal., and this amount is sufficient to enable the atom to reunite with a molecule of trithionate to tetrathionate, or with the latter to form pentathionate. The near approach to equality of the differences in the last column suggests that the different sulphur atoms are really of equal thermochemical value.

The reactions represented by the equations (1), (2), and (3) on p. 319, *occur under the same chemical and physical conditions and take place in the same liquid.* From this it follows of necessity that in a solution containing potassic tri-, tetra-, and penta-thionate decomposition and re-formation of these salts must be continuously going on, that is to say, the sulphur atoms are in uninterrupted migration from salt to salt.

The molecules of liquids are regarded as being in a state of continual motion—translatory, rolling one over the other, and rotating round their centres of gravity (Clausius, *Abhandlungen*, 1867, **2**, 237). The colliding molecules must come in this way in variable positions towards each other. Not every relative position of 2 mols. enables them to enter into chemical reaction, but of all positions which 2 mols. can assume towards each other, there will be one more favourable to chemical action than the others. This relative position of 2 mols. towards each other I will call their "position of reaction."

Whenever 1 mol. of potassic pentathionate meets a molecule of potassic trithionate in the *position of reaction*, 2 mols. of potassic tetrathionate will be the result of their interaction (p. 319), or if a molecule of potassic pentathionate meets with one of tetrathionate in the *position of reaction* the transfer of a sulphur-atom from the pentathionate to the tetrathionate will follow. The penta- becomes tetra-, and the tetra- penta-thionate.

Two molecules of potassic tetrathionate in their *position of reaction* produce one of trithionate and one of pentathionate.

Like a pendulum which during its fall acquires the necessary *vis viva* to rise again to a height equal to that of its descent, so the sulphur atoms of one polythionate acquire during decomposition the necessary energy to combine with another polythionate. The decomposition represented by the equations mentioned before, and the conditions under which they occur, require of necessity the migration of one sulphur atom of potassic tetrathionate and of two sulphur atoms of potassic pentathionate between the molecules of the potassic polythionates; but they also point out that after some time a certain transient ratio between the quantities of the polythionates will be established. This will occur if in a unit of time, as much of each of the salts present is re-formed as is decomposed.

If one of the three polythionates, penta-, tetra-, or tri-thionates, is dissolved in water, the solution will, after some time, contain all three, and their relative quantities will depend on the conditions just stated.

If this state of equilibrium between the formation and decomposition of the polythionates could be maintained, then the relative quantities of the different salts would remain unaltered. But this cannot be on account of the decomposition of potassic trithionate into potassic sulphate, sulphurous acid, and sulphur, a chemical change which cannot be reversed. The oxidation of the sulphurous to sulphuric acid, which prevents the decomposition of penta- and tetra-thionate, exercises also in course of time a disturbing influence. As soon as a certain amount of hydric sulphate has accumulated, the spontaneous decomposition of potassic penta- and tetra-thionate will cease, but that of potassic trithionate will go on. Hence the final state of equilibrium which ought to result after a long time (several months) would be potassic sulphate, hydric sulphate, sulphur, potassic tetrathionate, and potassic pentathionate, each of them in certain fixed quantity and not undergoing further chemical change.

Another important conclusion following from the equations (p. 319) is, *that in spite of the liquid condition, the molecules come comparatively seldom into the position of reaction.*

Equation (2) is only partially realised after a 10 per cent. solution

of potassic tetrathionate has been kept for 12 days. In this transformation, no external energy has to be introduced, the internal forces are sufficient for the purpose, and, nevertheless, it proceeds very slowly, probably for the reason given.

But if the molecules, although they are in the liquid state, only seldom assume *the position of reaction* towards each other, *then they cannot be so movable amongst each other as is commonly assumed*, they must have a tendency, dependent on their chemical nature, to set themselves in certain positions towards each other, and these positions need not be the *positions of reaction*. A solution of potassic pentathionate decomposes by degrees into potassic tetrathionate and sulphur. If a molecule of sulphur contains only six atoms of sulphur, and if the composition of potassic pentathionate in solution is the same as in the dry state, then 3 mols. of hydrated potassic pentathionate must come into the *position of reaction* in order to decompose according to the equation—

$$3[2K_2S_5O_6,3H_2O] = 6K_2S_4O_6 + S_6 + 9H_2O.$$

The slowness of this decomposition indicates that the *position of reaction* is *not often* assumed by the molecules of potassic pentathionate.

If now we consider molecules of potassic tetrathionate placed between the molecules of the pentathionate, then the decomposition of the latter ought to be further retarded. The mere presence of tetra-molecules between the penta-molecules would be a mechanical hindrance to the latter to meet in the *position of reaction*, and the tetra-molecules would also have a tendency to combine with sulphur in *statu nascendi* set free by the decomposition of potassic pentathionate, and with this sulphur again to form potassic pentathionate, thus restoring the original state of things.

To test this conclusion, the following experiments were made. Four solutions were prepared of the following composition:—

I. 0·6 gram of potassic pentathionate in 10 c.c. of water.

II. 0·6 gram of potassic pentathionate and 0·5 gram potassic tetrathionate in 10 c.c. of water.

III. 0·6 gram of potassic pentathionate and 2·5 grams of potassic tetrathionate in 15 c.c. of water, 1 mol. of $K_2S_5O_6$ and 5 mols. $K_2S_4O_6$.

IV. 0·483 gram of potassic pentathionate and 4·09 grams of potassic tetrathionate in 15 c.c. of water, or 1 mol. of $K_2S_5O_6,1\frac{1}{2}H_2O$ + 10 mols. $K_2S_4O_6$.

The solutions were perfectly clear and neutral, and were placed in

corked tubes in the same test-tube stand. After the lapse of 10 days, the following changes had taken place :—

I and II had deposited a small precipitate of sulphur, III and IV were still clear, and, like I and II, neutral.

After the lapse of 14 days, an increase in the quantity of the sulphur precipitate in I and II was noted; I was still neutral, II slightly acid. Some of the potassic tetrathionate of II had decomposed into sulphur and trithionate, and some of the latter into potassic sulphate, sulphur, and sulphurous acid.

III was still clear, but slightly acid, and produced with baric chloride a little baric sulphate. No odour of sulphurous acid was perceptible.

IV was slightly turbid, smelt of sulphurous acid, and gave a copious precipitate with baric chloride.

The sulphur of I and II was collected on weighed filters.

I gave 0·020 gram.
II only 0·004 „

That is to say, the solution of pure potassic pentathionate had deposited in 14 days five times as much sulphur as the solution which contained for every molecule of potassic pentathionate a molecule of potassic tetrathionate, or two-fifths of the pentathionate of I and only two twenty-fifths of that salt of II were decomposed. Solution III was still clear after the lapse of 21 days, and free from the smell of sulphurous acid, but IV now contained much precipitated sulphur and also free sulphurous acid.

In the course of the fourth week, sulphur and sulphurous acid also appeared in Solution III.

In another series of experiments with three solutions, of which the first contained only potassic pentathionate, the second in addition to every molecule of pentathionate a molecule of tetrathionate, and the third 2 mols. of tetrathionate to 1 of pentathionate, similar results were obtained. After the lapse of seven days, much sulphur was found in the solution of pure potassic pentathionate, considerably less in the solution which contained an equal number of molecules of both salts, and none at all in the liquid in which the molecular ratio of penta- to tetra-thionate was as 1 to 2.

These experiments prove that the decomposition of potassic pentathionate into potassic tetrathionate and sulphur is retarded by the presence of potassic tetrathionate, and that the degree of retardation is dependent on the quantity of potassic tetrathionate.

The retardation was greatest in the above experiments, when the solutions contained 1 mol. of potassic pentathionate to 5 mols. of the tetrathionate. The decomposition became accelerated again when

10 mols. of tetrathionate were mixed with 1 mol. of pentathionate, because the chemical change represented by equation (2) (p. 319) tends to increase the quantity of the potassic pentathionate. By means of similar experiments, it was proved that the decomposition of potassic tetrathionate expressed by equation (2) (p. 319) is retarded by the presence of potassic pentathionate.

The cause of this influence is easily seen. If we add potassic pentathionate to a solution of potassic tetrathionate, which is partially decomposed according to the equation—

$$2K_2S_4O_6 = K_2S_5O_6 + K_2S_3O_6,$$

with formation of potassic trithionate, then the sulphur liberated by the spontaneous decomposition of the pentathionate—

$$K_2S_5O_6 = K_2S_4O_6 + S,$$

will combine with the trithionate, and reproduce tetrathionate, and so prevent the decomposition expressed by the equation—

$$K_2S_3O_6 = K_2SO_4 + SO_2 + S.$$

Not less intelligible is the fact that for a certain proportion of the two salts, potassic tetra- and penta-thionate, the rate of change will be a minimum, and if one of these two salts is present in greater proportion, its peculiar decomposition will preponderate, and thereby increase the rate of change.

It has been shown that hydric sulphate prevents the spontaneous decomposition of potassic penta- and tetra-thionates. A certain proportion of the sulphate, about 2 per cent., is sufficient for this purpose, and its action consists in preventing the molecules of these polythionates from assuming towards each other the *position of reaction*.

The hydric sulphate has a polarising action on the molecules, and, perhaps in a similar way, it acts on the molecules of water in electrolysis.

Explanation of two Properties of Ozone.

Ozone and potassic pentathionate resemble each other in some respects; both undergo slow spontaneous decomposition. Acids render them more stable.* Alkalis cause rapid chemical decomposition, oxygen is given off from ozone, and sulphur from potassic pentathionate.† Both the oxygen liberated from ozone and the sulphur from the pentathionate were in endothermic combination.

* V. Babo, *Gmelin-Kraut Handbook*, 1, 26; Jeremin, *Jahresbericht*, by Liebig, &c., 1878, 197. This paper, p. .

† Soret, *Gmelin-Kraut*, 1 and 2, 27. This paper, p. 311.

An aqueous solution of potassic pentathionate decomposes very slowly into potassic tetrathionate and sulphur. Ozone by degrees, at common temperatures, returns to the condition of ordinary oxygen,* and both transformations agree in this respect, that they are not complete after the lapse of six months. The explanation given of the spontaneous decomposition of potassic pentathionate may, therefore, with a high degree of probability, be applied to the slow chemical change of ozone.

Concentrated solutions of potassic pentathionates decompose with greater rapidity than weak ones, and oxygen highly charged with ozone loses the latter more quickly than gas which contains a smaller quantity of ozone. Whenever 2 mols. of ozone meet under favourable conditions, that is to say, when they come into such a position that an oxygen atom of one can combine with an oxygen atom of the other, or, in other words, when they come in the *position of reaction*, then 2 mols. of ozone will be transformed into 3 mols. of common oxygen. This will happen more frequently in a gas which contains a larger than in one with a smaller number of ozone molecules. The 2 mols. which participate in this reaction are of comparatively simple structure, so that we may assume that every collision brings them into the *position of reaction*, and causes their conversion into oxygen.

Not two, but perhaps six or more molecules of potassic pentathionate, molecules of complex structure, must collide in the *position of reaction*, in order to produce a molecule of sulphur and potassic tetrathionate. This will, *à priori*, not happen in every collision, as in the case of ozone, and consequently we arrive at the conclusion that the spontaneous decomposition of potassic pentathionate into sulphur and potassic tetrathionate will be a much slower process than the transformation of ozone into oxygen. The facts are in perfect accord with this conclusion.

Ozone, if kept, will become richer in oxygen, and poorer in ozone, at first rapidly, afterwards, as the quantity of oxygen becomes larger, more and more slowly, until at last a small residue of ozone appears to undergo no further diminution (Berthelot).

Brodie (*Phil. Trans.*, 1872, 445) observed that ozonised oxygen when kept lost nearly one-third of its ozone in the first 90 hours. The loss during this interval of time was by no means uniform, but diminished rapidly towards the close. It amounted during the first 66 hours to nearly $\frac{1}{13}$, and during the next 24 hours only to $\frac{1}{26}$ of the original quantity. The oxygen molecules, as they increase in numbers and move between the ozone molecules, diminish the frequency of collision between the latter, and the consequent production of oxygen, just as

* Andrews and Tait, *Gmelin-Kraut*, 1 and 2, 26; Berthelot, *Jahresbericht*, 1878, 197; Brodie, *Phil. Trans.*, 1872, 445.

potassic tetrathionate retards the decomposition of potassic pentathionate. And applying the explanation of the chemical action between these two salts to ozone and oxygen, we arrive at the conclusion that the oxygen molecules during their motion of translation, and consequent collisions with ozone molecules, take an atom of oxygen from the latter, and thus become ozone molecules, and the ozone molecules in consequence of this loss will become oxygen molecules. Expressed in other words, in ozonised oxygen the ozone is continually decomposed and re-formed, or oxygen *atoms* migrate between oxygen and ozone molecules. In the same way, as has been shown, a sulphur atom passes from a molecule of potassic pentathionate to a molecule of potassic tetrathionate, the latter becoming penta- and the former tetra-thionate.

The conversion of ozone molecules into oxygen molecules during the keeping of ozonised oxygen, as well as the retardation of this process as a consequence of an increase of the quantity of the oxygen of the mixture, are, I think, fully explained by the theoretical views described. But also the fact that the amount of ozone in oxygen cannot be increased beyond a certain limit can be deduced from the same conceptions. The oxygen molecules are split into atoms by electricity, and the atoms so set free combine with oxygen molecules to form ozone. The ozone molecules by their collisions again form oxygen molecules. The limit beyond which oxygen cannot be changed to ozone is attained when in a given time as much ozone is reproduced in one operation as is decomposed in the other.

Explanation of the Decomposition of Peroxide of Hydrogen.

This substance comports itself in a chemical sense very much like ozone and pentathionates. An aqueous solution of peroxide of hydrogen contains less of the latter substance a few months after preparation than it did at first, probably in consequence of decomposition, according to the equation—

$$2H_2O_2 = 2H_2O + O_2.$$

This decomposition proceeds more rapidly in concentrated than in weak solutions, and is accelerated by a rise of temperature.*

A solution which in one litre contained 3·85 grams of active oxygen, in 87 days lost 3·678 grams, but was not completely decomposed after two years. Older samples had lost all their peroxide of hydrogen. This behaviour is very like that of a solution of potassic pentathionate,

* Berthelot, *Jahresbericht*, 1880, p. 136; also according to my own observations.

and both substances are endothermic compounds. Whenever 2 mols. of peroxide of hydrogen meet in the *position of reaction*, then decomposition into water and oxygen will take place, but if they collide in other positions, then they will not decompose.

From this tenet the properties of peroxide of hydrogen mentioned before can be deduced. The spontaneous decomposition will be retarded when water molecules are placed between the molecules of peroxide of hydrogen, and the retardation will increase with the quantity of water. A weak solution of peroxide of hydrogen is more stable than a concentrated one.

The similarity which exists between the spontaneous decompositions of potassic pentathionate and peroxide of hydrogen justifies the assumption that peroxide of hydrogen and water comport themselves towards each other like potassic pentathionate and tetrathionate.

It has been proved that an atom of sulphur can separate from pentathionate and unite with tetrathionate (p. 323). By analogy, then, we conclude that when a molecule of water and a molecule of peroxide of hydrogen during collision assume the *position of reaction*, the water will become peroxide of hydrogen, and the peroxide of hydrogen water, that is to say, an atom of oxygen will migrate from one molecule to another. The peroxide of hydrogen in an aqueous solution is therefore in a continuous state of decomposition and formation, however, in such a way, that for each state of concentration the amount of decomposition (very small in weak solutions) prevails over the amount of formation in the same time.

The decomposition of peroxide of hydrogen into water and oxygen is retarded by some and accelerated by other substances. Platinum, silver oxide, and manganic dioxide, respectively, promote, whilst acids prevent the decomposition. Platinum possesses a great attraction for oxygen, its powder absorbs more than 200 times its volume of the gas. This attraction is also exerted towards oxygen which is in chemical combination.

If now a piece of platinum is placed in peroxide of hydrogen, the molecules of the latter will place themselves in such a position on the surface of the platinum, that one oxygen-atom of the peroxide is turned towards the platinum and as near to it as possible. The peroxide is polarised. But this has the effect also of bringing the oxygen-atoms of different molecules of peroxide in such close proximity on the surface of the metal that they can combine to form common oxygen, the decomposition of the peroxide into water and oxygen and development of energy being the consequence. The action of the platinum places the molecules of the peroxide in *the position of reaction* towards each other. The action of silver oxide and of black oxide of manganese are similar.

Similar observations can be made on the aqueous solutions of the oxides of chlorine, &c. (Williamson, *Annalen*, **54**, 133).

The Action of Hydric Sulphide on Pentathionates.

2·95 grams of potassic pentathionate were dissolved in 20 c.c. of water, and a very concentrated solution of 2·458 grams of dihydric tartrate added. The precipitated potassic hydric tartrate was, after two days' standing, removed by filtration and a slow current of hydric sulphide passed for half an hour through the clear filtrate. The liquid was now put aside in a well-stoppered cylinder for 24 hours. The smell of hydric sulphide had disappeared after the lapse of this time. This treatment with hydric sulphide was repeated several times until all the hydric pentathionate was decomposed.

The result of these operations was a copious precipitate of sulphur and a clear colourless liquid. *Only a trace of trithionic acid could be discovered in this liquid.* Hydric pentathionate and hydric sulphide therefore form water and sulphur:—

$$H_2S_5O_6 + 5H_2S = 6H_2O + 10S.$$

The non-production of hydric sulphate is interesting.

An aqueous solution of 10·3 grams of potassic pentathionate was treated like hydric pentathionate with hydric sulphide, until no further action appeared to take place. A copious precipitate of sulphur had collected, which was separated by filtration and the filtrate carefully examined. Potassic trithionate and potassic thiosulphate were detected and obtained in crystals by evaporation.

The reactions are probably represented by the following equations:—

$$K_2S_5O_6 + H_2S = K_2S_3O_3 + H_2S_2O_3 + S_2$$
$$H_2S_2O_3 = SO_2 + H_2O + S$$
$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S,$$

and these united:—

$$3K_2S_5O_6 + 3H_2S = K_2S_2O_3 + 2K_2S_3O_6 + 3H_2O + 10S.$$

Action of Hydric Sulphide on Tetrathionates.

A solution of pure hydric tetrathionate, prepared by the same method as that by which the corresponding pentathionate had been obtained, was treated repeatedly with hydric sulphide till the decomposition appeared to be complete.

Less sulphur was precipitated in these operations than in the corresponding experiments with hydric pentathionate. In the resulting liquid, hydric pentathionate alone could be discovered. From this it

appears that hydric tetrathionate decomposes with hydric sulphide into water and sulphur:—

$$H_2S_4O_6 + 5H_2S = 6H_2O + 9S.$$

Some of the sulphur in *statu nascendi* combines with hydric tetrathionate, to form hydric pentathionate. If the treatment with hydric sulphide had been continued long enough, only water and sulphur would have been obtained.

Action of Hydric Sulphide on Trithionates.

Hydric sulphide acts on potassic trithionate only very slowly, much more slowly than on pentathionates or tetrathionates. A solution of potassic trithionate saturated with hydric sulphide had to stand three days before all the hydric sulphide was decomposed. The odour of sulphurous acid could then be perceived, and a precipitate of sulphur had fallen down. The liquid was separated from the sulphur and examined after it had undergone four treatments with hydric sulphide. Potassic thiosulphate, potassic sulphate, and sulphur were the only products of decomposition found:—

$$2K_2S_3O_6 + 5H_2S = K_2SO_4 + K_2S_2O_3 + 5H_2O + 8S.$$

Hydric trithionate was prepared from the barium salt, and the latter from a Wackenroder's solution which contained some free sulphurous acid and baric carbonate. The baric pentathionate and tetrathionate were deprived by the baric sulphite respectively of two and of one atom of sulphur and converted into baric trithionate, the baric sulphite itself becoming baric thiosulphate.

Analysis of the baric trithionate:—0·3915 gram dried over hydric sulphate and oxidised with bromine-water produced 0·259 gram, and the filtrate on addition of baric chloride 0·505 gram of baric sulphate. 100 parts of the salt contain, according to these numbers, 38·88 parts of barium and 26·89 parts of sulphur. The formula $2BaS_3O_6 + 3H_2O$ requires 38·48 parts of barium and 26·97 parts of sulphur. The atomic ratio is—

$$Ba : S = 1 : 2·94.$$

5·942 grams of this salt were dissolved in 50 c.c. of water and precipitated with 1·687 gram of hydric sulphate. The filtrate from the baric sulphate measured 75 c.c., and comported itself with reagents like hydric trithionate.

Twenty-four hours after preparation, the filtrate had acquired the odour of sulphurous acid and a precipitate of sulphur had fallen down. The latter was separated by filtration, and the clear liquid placed under

a bell-jar over pieces of potassic hydroxide. The sulphurous acid volatilised in the course of two days, but another precipitate of sulphur was found in the liquid. Put back into a closed bottle, the odour of sulphurous acid reappeared in one or two days. These observations indicate that hydric trithionate is, at common temperatures, in a slow state of decomposition. After several weeks, undecomposed hydric trithionate could still be detected by means of a qualitative examination.

Two days after the preparation of the hydric trithionate, no hydric pentathionate could be detected in it, but after the lapse of 14 days, considerable quantities of it and also of hydric sulphate were observed.

The equation—

$$H_2S_3O_6 = H_2SO_4 + SO_2 + S,$$

represents the slow decomposition of the solution. But the sulphur does not all separate in the free state, a portion unites with undecomposed hydric trithionate, forming hydric pentathionate and probably hydric tetrathionate. The solution of hydric trithionate behaves in the same manner during evaporation on the water-bath, only the decomposition is much more rapid. But even after the solution has been evaporated to $\frac{1}{5}$ of its original volume, and has parted with much sulphur and sulphurous acid, undecomposed hydric trithionate can be detected in it. I concluded from these observations that hydric trithionate would be easily decomposed by hydric sulphide. Experiment proved this conclusion to be erroneous. A solution of hydric trithionate was saturated with sulphuretted hydrogen immediately after its preparation, and kept in a closed bottle for three days. No change could be observed, the liquid seemed to contain after this lapse of time as much hydric sulphide as it did immediately after the passage of the gas. Over pieces of potassic hydroxide under a bell-jar, it lost, in a few days, the sulphuretted hydrogen and a little sulphur was precipitated. The qualitative examination revealed the presence of some hydric sulphate and hydric pentathionate besides the hydric trithionate.

A second experiment gave similar results. Hence it appears that hydric trithionate is not acted upon by hydric sulphide at common temperatures.

Hydric pentathionate and hydric tetrathionate are easily decomposed by hydric sulphide; hydric trithionate, a far less stable compound, which slowly evolves sulphurous acid, is not acted on. The explanation of this anomaly appears to me to be as follows :—

Hydric tetra- and penta-thionate produce with hydric sulphide water and sulphur but *no hydric sulphate*. The hydrogen of the hydric sulphide reacts with the oxygen of these compounds. During

their spontaneous decomposition in aqueous solutions sulphur is separated but no sulphate is produced. An aqueous solution of hydric trithionate, on the other hand, is continuously in a slow state of decomposition with formation of hydric sulphate. The arrangement of the atoms in the trithionate must be such that the affinity of sulphur for oxygen is easily satisfied. In the case of a solution of hydric trithionate saturated with hydric sulphide, two influences make themselves felt. On the one hand, the affinity of the sulphur atoms for the oxygen atoms, and on the other hand the affinity of the hydrogen of the hydric sulphide for the oxygen of the trithionate. These two attractions are opposed to and counterbalance each other, so that a solution of hydric trithionate saturated with hydric sulphide is according to experiment more stable than one of pure hydric trithionate. A different result is obtained where hydric sulphide is passed into a mixture of the three polythionates, hydric trithionate, hydric tetrathionate, and hydric pentathionate. The hydric trithionate quickly disappears. Sulphuretted hydrogen and hydric tetra- or pentathionate produce water and sulphur. Sulphur in *statu nascendi* combining with hydric trithionate forming respectively tetrathionate and pentathionate.

From the foregoing observations, the conclusion may be drawn, that if a current of sulphuretted hydrogen is passed through a Wackenroder's solution in which hydric trithionate, hydric tetrathionate, and hydric pentathionate are present until the gas ceases to act on the solution, water and sulphur will be the final products of decomposition.

This conclusion was verified by experiment.

The equation—

$$2H_2S + SO_2 = S_3 + 2H_2O,$$

by which the text-books represent the chemical action between hydric sulphide and sulphurous acid is correct for the final products of the reactions.

The polythionates are intermediate products between the original materials, sulphurous acid, sulphuretted hydrogen and water on the one hand, and sulphur and water, the fixed products, on the other.

Action of Sulphurous Acid on Polythionates.

Action of Sulphurous Acid on Hydric Pentathionate.

Sulphurous acid partially converts hydric pentathionate into hydric trithionate. The solution of hydric pentathionate was obtained by the precipitation of potassic pentathionate with hydric tartrate as described on p. 328. One volume of the liquid so prepared was mixed

with two volumes of concentrated hydric sulphite. The colourless liquid became intensely yellow in the course of three hours and during the following two days deposited some sulphur. After it had been kept in a closed bottle for three days, it was placed over pieces of potassic hydroxide under a bell-jar, and allowed to remain till all the sulphurous acid had volatilised and combined with the base. Sulphur was precipitated whilst the sulphurous acid was escaping, and the yellow liquid became colourless. After all the sulphurous acid was gone, a qualitative examination of the remaining liquid proved the presence in it of hydric trithionate and hydric pentathionate. The action of sulphurous acid on hydric pentathionate may therefore be explained as follows: The sulphurous acid withdraws sulphur from the pentathionate, forming a yellow solution. This solution of sulphur in sulphurous acid deposits some of its sulphur in the form of a precipitate when it is left standing in a closed bottle, or during the volatilisation of the sulphurous acid. The pentathionate from which the sulphur has been taken by the sulphurous acid, becomes in consequence hydric trithionate. The sulphur unites with the sulphurous acid with a very feeble force, the compound behaving like a simple solution of sulphur in sulphurous acid. I will assume that this compound, which we shall have to consider again, is thiosulphuric or hyposulphurous acid, S_2O_2:—

$$H_2S_5O_6 + 2SO_2 = H_2S_3O_6 + 2S_2O_2.$$

This decomposition is, however, incomplete, even a *large excess* of sulphurous acid does not convert all the pentathionate into trithionate. Probably, therefore, the reaction is of a reciprocal nature, and the hydric trithionate can receive from thiosulphuric acid, S_2O_2, sulphur, and re-form hydric pentathionate.

Action of Sulphurous Acid or Sulphites on Potassic Pentathionate.

10 grams of potassic pentathionate dissolved in 30 c.c. of hydric sulphite to a yellow liquid. Baric carbonate was now added until all the acid was neutralised. Instead of baric sulphite, baric thiosulphate was obtained as an abundant crystalline precipitate. The filtrate from the sparingly soluble baric thiosulphate was freed from barium by careful addition of potassic carbonate, and then concentrated for crystallisation. Crystals of pure potassic trithionate were obtained.

No potassic pentathionate could be detected, the reaction with metallic salts, like those of potassium or barium, therefore, is complete.

The reactions can be represented by the following equations:—

$$K_2S_5O_6 + 2SO_2 = K_2S_3O_6 + 2S_2O_2, \text{ and}$$
$$2BaCO_3 + 2S_2O_2 = 2BaS_2O_3 + 2CO_2.$$

Action of Dipotassic Sulphite on Potassic Pentathionate.

4 grams of pure potassic pentathionate dissolved at 17° in 20 c.c. of water with a reduction of 3° of temperature. The solution was mixed with one of pure dipotassic sulphite, K_2SO_3. A considerable quantity of *sulphurous acid* was set free, and a small precipitate of sulphur formed. Addition of barium chloride caused the precipitation of a large amount of baric thiosulphate. The proportionally large quantity of the latter, and the evolution of much sulphurous acid, lead to the conclusion that dipotassic sulphite is decomposed by water into potassic hydroxide and sulphurous acid, and that the potassic hydroxide decomposes the potassic pentathionate according to the equation—

$$2K_2S_5O_6 + 6KHO = 5K_2S_2O_3 + 3H_2O.$$

Action of Sulphurous Acid on Hydric Tetrathionate.

The hydric tetrathionate was prepared by double decomposition of potassic tetrathionate and hydric tartrate. One volume was mixed with two volumes of a concentrated solution of sulphurous acid. The mixture was still colourless three hours after preparation, and turned yellow in the course of the three following days, but *without separation of sulphur.* Placed over pieces of potassic hydroxide under a bell-jar for the removal of the sulphurous acid, the yellow colour disappeared with the sulphurous acid, but without the precipitation of sulphur (p. 332). The examination of the liquid after the sulphurous acid was gone proved the presence of much hydric trithionate and hydric pentathionate. The sulphurous acid had acted on the tetrathionate in the same way that it does on the pentathionate, it had taken away sulphur from the hydric tetrathionate, and thus converted the latter into hydric trithionate. But the thiosulphuric acid, S_2O_2, instead of precipitating sulphur during standing or during evaporation of the sulphurous acid, gave up half its sulphur to hydric trithionate or undecomposed hydric tetrathionate, thus causing the formation of hydric pentathionate. The reciprocal nature of the reaction, mentioned as an explanation on p. 332, is thus confirmed.

Action of Sulphurous Acid on Wackenroder's Solution.

A sample of this solution, which did not contain sulphuretted hydrogen or sulphurous acid, was used for the following experiments, without concentration on the water-bath.

To a small portion some cupric sulphate was added. The δ-sulphur in solution as well as the sulphur in suspension were precipitated.

The filtrate of this precipitate remained clear at 100°, hence hydric trithionate was not present.

From another portion, the colloïdal sulphur was precipitated by a solution of saltpetre, and the filtrate from the sulphur tested with an ammonia-silver nitrate solution. Much hydric pentathionate was discovered. Tetrathionate and hexathionate were also present. Some of this Wackenroder solution was mixed with twice its volume of a concentrated solution of sulphurous acid. The mixture was then divided into two portions, one portion was placed over pieces of potassic hydroxide under a bell-jar, the other portion tested with cupric sulphate. A considerable dark-brown precipitate was obtained indicating much hydric trithionate. Sulphurous acid solution or the Wackenroder solution, each heated with cupric sulphate to 100°, remained unchanged.

The portion of the mixture of sulphurous acid and Wackenroder solution, which had been placed over pieces of potassic hydroxide, was likewise tested with cupric sulphate after the volatilisation of the sulphurous acid. No precipitate was obtained at 100°, consequently no hydric trithionate or hydric thiosulphate was present.

The sulphur which had been withdrawn from hydric tetrathionate or hydric pentathionate by the sulphurous acid, had again united with the hydric trithionate during the volatilisation of the sulphurous acid, thus re-forming hydric tetrathionate and hydric pentathionate. Another portion of a mixture of Wackenroder solution and hydric sulphite was allowed to stand 24 hours in a closed bottle before it was placed under a bell-jar over pieces of potassic hydroxide. After the volatilisation of the sulphurous acid, considerable quantities of hydric trithionate were discovered by means of cupric sulphate.

Another larger portion of Wackenroder's solution was saturated with sulphurous acid gas, and then left to stand five days in a closed bottle. The liquid was perfectly clear and yellow at the end of this time, the colloïdal sulphur having precipitated. It contained, however, much sulphur in the form of thiosulphuric acid, S_2O_2 (p. 332).

I will mention here a few more observations on the properties of this combination of sulphur and sulphurous acid.

If left to stand for a long time, sulphur will continually but slowly separate from it. The yellow colour becomes paler in consequence. But it appears to require many months before all the sulphur will precipitate in this manner.

The addition of water causes no precipitation of sulphur. Hydric chloride, hydric sulphate, potassic nitrate, sodic chloride, respectively do so with decoloration of the solution. The same effect follows the volatilisation of the sulphurous acid, either spontaneously at common temperatures or by boiling. I have not been able to separate this

compound from the solution, it seems to exist only in presence of free sulphurous acid. Neutralisation with baric carbonate throws down baric thiosulphate as a precipitate, leaving baric trithionate in solution. A precipitate so obtained was almost entirely soluble in boiling water, and the solution gave crystals of baric thiosulphate on evaporation.

0·664 gram of the crystals dried over hydric sulphate, and oxidised with bromine-water, gave 0·596 gram baric sulphate, and the filtrate with baric chloride 0·584 gram of the same salt.

Hence in 100 parts :—

	Found.	Theory. $3BaS_2O_3 + 2H_2O$.
Barium	52·72	52·49
Sulphur.....	24·40	24·52

For this reason I regard the yellow solution of sulphur in sulphurous acid as thiosulphuric acid, S_2O_2.

The filtrate of the baric thiosulphate gave a crystalline precipitate with alcohol.

I. 0·739 gram of this precipitate left after ignition 0·482 gram baric sulphate.

II. 0·573 gram gave 0·376 gram baric sulphate.

III. 0·283 gram oxidised with bromine-water gave 0·185 gram baric sulphate, and the filtrate on addition of baric chloride again 0·360 gram of the same salt.

Hence in 100 parts :—

	Found.			Theory.
	I.	II.	III.	$2BaS_3O_6 + 3H_2O$.
Barium ..	38·28	38·59	38·28	38·48
Sulphur..	—	—	26·45	26·96

If Wackenroder's solution contains, besides its usual constituents hydric pentathionate, hydric tetrathionate, and hydric hexathionate, a sufficient quantity of sulphurous acid, then only baric thiosulphate and baric trithionate are obtained after neutralisation with baric carbonate. This behaviour probably explains the results obtained by Curtius.

These observations and experiments explain perfectly the action of sulphurous acid on a Wackenroder solution. Immediately after the mixture has been prepared, some of the hydric pentathionate and hydric tetrathionate are reduced by the sulphurous acid to trithionate, the sulphurous acid itself forming thiosulphuric acid, S_2O_2, with sulphur. If now at once, or very soon after the preparation of the mixture, volatilisation of the sulphurous acid takes place, then half the sulphur of the thiosulphuric acid, S_2O_2, will reunite with the trithio-

nate, forming hydric tetrathionate and hydric pentathionate, and the original state of things is re-established. But if the mixture is allowed to stand for some time, one or more days, before the volatilisation of the sulphurous acid, then a portion of the sulphur of the thiosulphuric acid, S_2O_2, will precipitate in one of the ordinary modifications.

If after such precipitation volatilisation of the sulphurous acid occurs, then the sulphur resulting from the decomposition of the remaining thiosulphuric acid, S_2O_2, is not sufficient to convert all the hydric trithionate into tetrathionate or pentathionate. After the evaporation of the sulphurous acid, the solution then contains hydric trithionate, as is shown by the following experiment. A portion of the Wackenroder's solution, charged with sulphurous acid, as mentioned on p. 334, was deprived of its sulphurous acid after five days' standing.

The qualitative examination revealed much hydric trithionate, and on account of the reciprocal nature of the reactions also hydric tetrathionate and hydric pentathionate. The yellow colour of another portion of the solution had almost disappeared a year afterwards, that is to say, nearly but not all the thiosulphuric acid, S_2O_2, was decomposed. After removal of the sulphurous acid by evaporation, hydric trithionate, hydric tetrathionate, hydric pentathionate, and hydric hexathionate were found in the remaining liquid.

Influence of Time on the Formation of Hydric Pentathionate.

To a saturated solution of sulphuretted hydrogen, a solution of sulphurous acid was gradually added, drop by drop, until the odour of hydric sulphide had disappeared. Every drop of sulphurous acid caused a precipitate of sulphur. The action, therefore, appears to be instantaneous, and the mixture ought not to contain either of the substances. A tube was now quite filled with the mixture, and the liquid poured from it into a larger vessel and shaken with air. The latter acquired the smell of sulphurous acid, and paper moistened with lead acetate turned brown when immersed in the air, consequently, small quantities of hydric sulphide and sulphurous acid can exist for some time in a liquid prepared as described, without mutual decomposition, revealing their presence by their usual odour. The experiment was now repeated in reversed order. A slow current of sulphuretted hydrogen was passed for 20 minutes through a saturated solution of sulphurous acid at 0°. After the lapse of 10 minutes, some of the liquid was shaken in a large vessel with air; the latter took up sulphurous acid gas, but not hydric sulphide. The liquid, however, turned a paper moistened with lead acetate brown. The latter reaction could not be obtained after 12 hours.

The same results were obtained after the liquid had been treated a second time for 20 minutes with sulphuretted hydrogen. After a third treatment with sulphuretted hydrogen, the sulphurous acid appeared to be decomposed. The liquid no longer smelt of sulphurous acid, but had a feeble odour of hydric sulphide. Also when the liquid was shaken with air, it did not acquire the smell of sulphurous acid. The feeble odour of hydric sulphide disappeared, however, after three hours' standing, and a strong smell of sulphurous acid could now be perceived.

Some of the liquid now shaken with air transferred to the latter both sulphurous acid and sulphuretted hydrogen, the former recognisable by its smell, and the latter by its action on paper moistened with lead acetate. Even eight days after these experiments, traces of sulphuretted hydrogen and sulphurous acid could be detected in the liquid.

Similar observations were made repeatedly.

The experiments described show that, although concentrated solutions of sulphurous acid and sulphuretted hydrogen react immediately, small quantities of these two substances can exist side by side in a Wackenroder solution for some time without decomposing each other.

An aqueous solution of sulphurous acid heated on a water-bath very soon loses all its acid. A similar solution mixed with sulphur powder requires a very *much longer* time for the volatilisation of the sulphurous acid. Between sulphur and sulphurous acid, a considerable attraction exists, which manifests itself under the circumstances described. The Wackenroder solution holds much colloïdal sulphur in suspension and solution, and this by its attraction for the sulphurous acid, may be the cause of the phenomena described. Perhaps also thiosulphuric acid, S_2O_2 (p. 332), may be present in a Wackenroder's solution, and by its slow decomposition into sulphur and sulphurous acid cause the reappearance of sulphurous acid some hours after the preparation of the Wackenroder's solution appears to be finished. The yellow compound of sulphur and sulphurous acid, which I have called thiosulphuric acid, plays an important part in the formation of hydric pentathionate.

A slow current of sulphuretted hydrogen was passed through 500 c.c. of a nearly saturated solution of sulphurous acid at 0°, 50 c.c. were taken out after the current had passed 25 minutes, and placed in a closed bottle, and another 50 c.c. were placed over pieces of potassic hydroxide under a bell-jar. Through the remaining 400 c.c. of the liquid, a slow current of sulphuretted hydrogen was again passed for 25 minutes, and then 50 c.c. were removed to a closed bottle, and another 50 c.c. put over potassic hydroxide.

The same operation was repeated three times. I had, consequently, five portions of liquid, of which No. 1 had been treated with sulphuretted hydrogen 25 minutes; No. 2, 50 minutes; No. 3, 85 minutes; No. 4, 120 minutes; No. 5, 180 minutes.

The last portion, No. 5, did not smell of sulphurous acid immediately after preparation, but did so two days later. It was then treated for several minutes with sulphuretted hydrogen, and after this did not again acquire the smell of sulphurous acid. Each of the other four portions contained much free sulphurous acid.

Each portion consisted of two parts, one kept by itself in a bottle, the other over pieces of potassic hydroxide under a bell-jar. The parts over potassic hydroxide had, in the course of two or three days, lost their free sulphurous acid. They were now examined for the constituents of Wackenroder's solution. The sulphur in suspension and in solution was precipitated by addition of a solution of potassic nitrate, and the clear filtrate of the precipitate tested with the reagents mentioned on pp. 297 and 298.

No. 1 contained only a very small quantity of hydric pentathionate and hydric trithionate. No. 2 contained more of both substances than No. 1, No. 3 more than No. 2, and No. 4 more than No. 3. No. 5 was richer in pentathionate and poorer in trithionate than No. 4.

Examination of the Portions which had been kept for a few Days in closed Bottles.

These exhibited remarkable differences from those which had been placed over potassic hydroxide immediately after preparation. The last named still possessed the character of an emulsion, containing much sulphur in suspension and solution. The portions which had been kept a few days in closed vessels were, with the exception of No. 5, clear and of yellow colour, and no longer held sulphur in suspension, nor did they show the slightest opalescence (p. 283). Nos. 1, 2, 3 and 4 still contained considerable quantities of sulphurous acid, and sulphur in combination with it as S_2O_2.

These differences were caused by the sulphurous acid, which, as will be remembered, precipitates the suspended and dissolved colloïdal sulphur in the course of a few days.

After having stood for five days in closed bottles, the five portions were placed over pieces of potassic hydroxide under a bell-jar. In proportion as the sulphurous acid volatilised and was absorbed by the potassic hydroxide, the solutions lost their yellow colour and deposited sulphur. After the lapse of 48 hours, they were colourless and free from sulphurous acid, as shown by the test with starch coloured blue by iodine. The odourless and colourless liquids

were now separated from the precipitated sulphur by filtration. The examination of the filtrates showed that Nos. 1, 2, 3 and 4 contained much more hydric pentathionate and trithionate than the corresponding portions, which had been placed over potassic hydroxide immediately after preparation. No. 1 of the latter set gave, with potassic hydroxide or ammonia-silver nitrate, only very feeble indications of the presence of hydric pentathionate. No. 1 of the set which had been kept five days in closed bottles, comported itself with the reagents like a concentrated solution of hydric pentathionate, and similar observations were made with regard to the quantities of hydric trithionate in the two sets of liquids. The examination of Nos. 2, 3 and 4 gave the same results. No. 5 again contained much less hydric trithionate than No. 4, but appeared to be richer in pentathionate.

Consequently, if a solution of sulphurous acid is partially decomposed by sulphuretted hydrogen, and then the residual sulphurous acid immediately removed by evaporation, a comparatively small yield of hydric pentathionate and hydric trithionate is obtained.

If, however, the solution is allowed to stand a few days before the volatilisation of the undecomposed sulphurous acid, then comparatively large quantities of the two polythionic acids mentioned are formed.

How is this unexpected result to be explained? The yellow solution of sulphur in sulphurous acid, or more probably combination of the two, which I have called thiosulphuric acid, S_2O_2, because it forms thiosulphates when neutralised with bases, and decomposes into sulphur and sulphurous acid when the latter can evaporate, seems to be the source of the hydric pentathionate.

The thiosulphuric acid is only stable in presence of a very large excess of sulphurous acid.

If the excess of sulphurous acid be not very large, then condensation of the thiosulphuric acid into pentathionic acid will take place by degrees :—

$$5S_2O_2 = 2S_5O_5,$$

and

$$2S_5O_5 + 2H_2O = 2H_2S_5O_6.$$

This condensation, dependent on the quantity of sulphurous acid present, requires days for its accomplishment, and does not occur at all if the sulphurous acid is in very large excess.

Therefore, we conclude, that if hydric sulphide be passed through a solution of sulphurous acid uninterruptedly till all the acid is decomposed, but little hydric pentathionate will be found in the resulting mixture. The following experiments were made with the view of testing this conclusion. In order to shorten the time of the experi-

ments, quantities of 120 c.c. of sulphurous acid only were operated upon at a time instead of 480 or 500 c.c. as on former occasions.

A slow current of sulphuretted hydrogen was passed through 120 c.c. of a saturated solution of sulphurous acid at a few degrees above 0°. The decomposition was complete in three and three-quarter hours.

Four operations of this description yielded 480 c.c. of Wackenroder's solution, which were evaporated on a water-bath until the residual liquid was of the sp. gr. 1·267. The filtrate from the coagulated sulphur measured 41 c.c. It was diluted to 52 c.c. and was then of the sp. gr. 1·24.

Reactions of this Filtrate.—It gave a bright yellow precipitate with mercurous nitrate (absence of hydric trithionate). Potassic hydroxide and ammonia-silver nitrate respectively reacted as with pentathionates, but with feeble intensity.

Analysis of the Filtrate.

I. 5 c.c. gave with baric chloride 0·281 gram of baric sulphate.

II. 5 c.c. were boiled for a few minutes with mercuric cyanide and digested at 100° for two hours.

The precipitate of mercuric sulphide and sulphur weighed 2·451 grams, and the filtrate from this precipitate gave with baric chloride 4·321 grams of baric sulphate. 0·324 gram of the precipitate by mercuric cyanide treated with bromine water gave 0·0425 gram of sulphur and 0·375 gram of baric sulphate, which together contain 0·094 gram of sulphur. The filtrate of the 0·375 gram of baric sulphate gave with hydric sulphide 0·266 gram of mercuric sulphide, containing 0·229 gram of mercury. 0·094 gram of sulphur + 0·229 gram of mercury = 0·323, consequently a loss of 0·001. This loss will probably be in the weight of the mercury; therefore, we take the mercury to be 0·230 gram. Hence, 2·451 grams of the precipitate caused by mercuric cyanide contain 0·711 gram of sulphur and 1·740 grams of mercury.

0·524 gram of the precipitate of mercuric sulphide and sulphur was oxidised with aqua regia, and gave on precipitation with baric chloride 1·08 gram of baric sulphate containing 0·1483 gram of sulphur.

The difference between the weight of the sulphur and the precipitate taken is equal to 0·3357 gram of mercury. According to this second experiment, 2·451 grams of the mercuric cyanide precipitate contain 0·694 gram of sulphur and 1·757 grams of mercury. The mean of both experiments is 0·702 gram of sulphur and 1·748 grams of mercury.

From these numbers we calculate—

$$SO_3 : Hg : S = 1{\cdot}984 : 1 : 2{\cdot}51,$$

and for the composition of the hydric polythionates of the Wackenroder solution analysed—

$$H_2S_{4{\cdot}49}O_{5{\cdot}95},$$

for which we adopt—

$$H_2S_{4{\cdot}5}O_6,$$

and for the mean composition of the acids,

$$S_{4{\cdot}5}O_5.$$

Preparation of the Potassium Salts.

The remaining 37 c.c. of the analysed solution were mixed with a concentrated solution of 12 grams of potassic acetate and the mixture placed on a plate in the window of a draught closet. The dry residue, obtained after 24 hours, weighed, after pressing between layers of filtering paper, 22 grams. It was moistened with some water and pressed again between paper, whereby it sustained a loss of 6 grams.

The remaining 16 grams were now dissolved in 30 c.c. of water acidulated with 15 drops of hydric sulphate, and separated by filtration from a few milligrams of sulphur. A few hours after filtration, the clear liquid deposited a trace of sulphur, and in the course of some days gave two crystallisations of potassic tetrathionate. These weighed 6 grams.

Reactions of these Crystals.

They formed with water a clear, colourless, neutral solution which, on addition of potassic hydroxide and ammonia-silver nitrate respectively, remained unchanged, but gave a bright yellow precipitate with mercurous nitrate.

Determination of Potassium.

0·831 gram gave 0·478 gram of potassic sulphate. Hence in 100 parts—

	Found.	Calculated. $K_2S_4O_6$.
Potassium.....	25·7	25·8

The salt, therefore, is potassic tetrathionate.

A third crystallisation also consisted of nothing but crystals of tetrathionate. The fourth and last crystallisation contained a few crystals of potassic pentathionate, which were picked out from the accompanying potassic tetrathionate.

The entire weight of the latter amounted to 9 grams, and of the penta-salt to 1·6 grams. Consequently, the yield of hydric pentathionate is much smaller when hydric sulphide is passed uninterruptedly through a solution of sulphurous acid till the latter is completely decomposed, than when the operation is conducted as described on page 281, with interruptions of from 36 to 48 hours, when nearly equal weights of the two potassium salts were obtained. These results confirm the theory mentioned on page 339.

Weak solutions of sulphurous acid appear to produce proportionately larger quantities of the polythionic acids than more concentrated solutions.

Experiment I.—A slow current of sulphuretted hydrogen was passed for two hours through 480 c.c. of a concentrated solution of sulphurous acid, and the liquid was allowed to stand for two days. The operation with sulphuretted hydrogen was then repeated for two hours and the solution allowed to stand for 48 hours.

The treatment with sulphuretted hydrogen was continued in this manner until all the sulphurous acid was decomposed, which was the case after two weeks.

Experiment II.—Only 120 c.c. of sulphurous acid was taken in the following preparation. The experiment was made in the same manner as the first, but required on account of the smaller quantity of acid much less time for its performance.

On the first day, hydric sulphide was passed for one hour and on the second for an hour and a half, the decomposition of the sulphurous acid was then complete.

Experiment III was made like Expt. II with 120 c.c. of sulphurous acid. In Expts. I and II the acid was of the same strength, in Expt. III an acid of half this strength was taken.

Experiment IV was performed like Expt. II, with this difference, that the sulphuretted hydrogen was passed uninterruptedly until all the sulphurous acid was decomposed.

The results calculated for the same quantity of sulphurous acid are as follows:—

Expt. I. 480 c.c. of sulphurous acid gave 65 c.c. of Wackenroder solution of sp. gr. 1·265.

Expt. II. 480 c.c. of sulphurous acid gave 55 c.c. of Wackenroder solution of sp. gr. 1·246.

Expt. III. 960 c.c. of sulphurous acid gave 55 c.c. of Wackenroder solution of sp. gr. 1·268

Expt. IV. 480 c.c. of sulphurous acid gave 41 c.c. of Wackenroder solution of sp. gr. 1·267.

Experiments I and II show that occasional interruptions of

from one to two days' duration in the passage of the sulphuretted hydrogen, and longer treatment with this gas, yield the largest quantity of acid. Expts. II and III indicate that it is of advantage to use a weak solution of sulphurous acid. Expt. IV shows that if sulphuretted hydrogen be passed through a solution of sulphurous acid uninterruptedly until it is completely decomposed, absolutely and relatively the smallest quantity of acid will be produced. The increase in the quantity of the hydric pentathionate, which takes place when a solution of sulphurous acid, which is only partially decomposed by sulphuretted hydrogen, is kept a few days, appears to be due to a condensation of thiosulphuric acid, S_2O_2, according to the equation—

$$5S_2O_2 + 2H_2O = 2H_2S_5O_6.$$

As the quantity of hydric tetrathionate seems to remain unchanged, and not to be dependent on this condition, it is probably formed by the direct union of the reacting bodies—

$$3SO_2 + H_2S = H_2S_4O_6.$$

If this theory be correct, then pentathionates ought to be formed generally by the action of sulphurous acid on sulphur in *statu nascendi*.

The results of the following experiments support this conclusion.

Action of Sulphurous Acid on Potassic Thiosulphate.

Five grams of potassic thiosulphate, $2K_2S_2O_3,3H_2O$, were dissolved in 100 c.c. of a concentrated solution of sulphurous acid. The intensely yellow solution could be kept *without* separation of sulphur or any other apparent change.

Hydric chloride caused decolorisation and precipitation of liquid sulphur, which in the course of a few days became solid and opaque. A portion mixed with two or three volumes of alcohol, gave a crystalline precipitate which was soluble in water, with the exception of some globules of sulphur.

The aqueous solution produced, on addition of baric chloride, a crystalline precipitate which was only partially soluble in boiling water. The dissolved portion was baric thiosulphate, the insoluble baric sulphate and sulphite. Other substances were not observed. From these experiments, it appears that potassic thiosulphate is decomposed by sulphurous acid into potassic sulphite and thiosulphuric acid, which remains unchanged in the large excess of sulphurous acid present (p. 339).

In another experiment, 5 grams of potassic thiosulphate were dissolved in only 5 c.c. of sulphurous acid. The yellow solution deco-

lorised in the course of three days, the smell of sulphurous acid disappeared, and sulphur was precipitated. A few c.c. of sulphurous acid were again added, when the same effects followed, the mixture turned yellow, and smelt of sulphurous acid, but lost both colour and odour with precipitation of sulphur in the course of a day or two. The addition of small quantities of sulphurous acid was continued until it ceased to produce coloration, and its odour permanent. Altogether 18 c.c. of sulphurous acid were used, and 0·153 gram of sulphur was precipitated. Sulphurous acid added in small quantities to potassic thiosulphate therefore, does not act like a large excess.

Absolute alcohol added to the decomposed solution of potassic thiosulphate, precipitated potassic trithionate, and in the filtrate from the latter *potassic pentathionate* was discovered by means of ammonia-silver nitrate. According to the text-books, potassic thiosulphate and sulphurous acid produce potassic trithionate and sulphur, as represented by the equation—

$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S,$$

which would require the precipitation of 0·368 gram of sulphur from 5 grams of potassic thiosulphate. Experiment gave only 0·153 gram, not half the calculated quantity.

The missing sulphur is in the form of *potassic tetrathionate* and *pentathionate* in the solution. The sulphurous acid decomposes a portion of the potassic thiosulphate into potassic sulphite and thiosulphuric acid, which by *condensation* is transformed into pentathionic acid. The latter and the potassium salts produce potassic pentathionate and sulphurous acid or thiosulphuric acid, which when very little sulphurous acid is present will partially decompose into sulphur and sulphurous acid.

Potassic sulphite and potassic pentathionate form potassic thiosulphate and potassic trithionate.

The final products of the action of sulphurous acid on potassic thiosulphate are potasssic trithionate as chief product, potassic tetrathionate and pentathionate, and sulphur. The reactions may be represented by the equation—

$$6K_2S_2O_3 + 9SO_2 = K_2S_3O_6 + K_2S_4O_6 + 4K_2S_3O_6.$$

In reality, less potassic pentathionate and tetrathionate and more potassic trithionate are produced on account of the precipitation of sulphur in quantities varying in different experiments.

In confirmation of the explanations given here of the action of sulphurous acid on potassic thiosulphate, I found that potassic pentathionate and sulphurous acid produce similar results, viz., potassic tetrathionate, trithionate, and sulphur. A third experiment gave

results similar to the second. A fourth experiment was made with a view of separating the potassic tetrathionate and pentathionate from the trithionate, and obtaining each salt in a pure form. 55 grams of potassic thiosulphate were treated with sulphurous acid until the whole quantity was converted into polythionates.

Alcohol precipitated potassic trithionate, the filtrate on standing deposited crystals of pure *potassic tetrathionate*, but gave by spontaneous evaporation crystals of all three salts interlaced in such a way that they could not be separated mechanically; an aqueous solution of the mixed salts, however, comported itself with the reagents like one of a pentathionate.

The precipitate of sulphur amounted to 4·86 per cent.

Chloride of Sulphur and Sulphurous Acid.

The view expressed on page 343 on the formation of pentathionates is also confirmed by the experiments of Plessy (p. 280), and Fordos and Gélis (p. 280). The salts prepared by these chemists were, however, not pure, and their analytical methods unsatisfactory. I have therefore repeated their experiments.

Sulphurous chloride, S_2Cl_2, and water decompose into hydric thiosulphate, sulphur, and hydric chloride—

$$2S_2Cl_2 + 3H_2O = H_2S_2O_3 + 4HCl + S_2.$$

The hydric thiosulphate, $H_2S_2O_3$, however, soon splits up into water, sulphur, and sulphurous acid. Gmelin (*Gmelin-Kraut*, **1**, Abth. II, 401) quotes a statement of Carius, according to which sulphurous chloride and water produce hydric chloride, sulphurous acid, and sulphuretted hydrogen:—

$$S_2Cl_2 + 2H_2O = 2HCl + SO_2 + H_2S.$$

The sulphuretted hydrogen and the sulphurous acid would form the constituents of Wackenroder's solution. This view of Carius (*Annalen*, **107**, 333 *et seq.*) of the decomposition of sulphurous chloride by water is entirely *hypothetical*, not supported by experiments, and has been advanced by him as an argument in favour of his view of the chemical constitution of the chlorides of sulphur.

Sulphurous chloride dissolves in an aqueous solution of sulphurous acid without precipitation of sulphur, but the smallest quantity of sulphuretted hydrogen produces, even with a very large excess of sulphurous acid, an *immediate* precipitate of sulphur. The formation of hydric sulphide required by the equation of Carius does not therefore occur. Accordingly I adopt the first explanation of the decomposition of sulphurous chloride by water.

30 grams of sulphurous chloride were introduced by degrees into 480 c.c. of a concentrated aqueous solution of sulphurous acid. The chloride of sulphur, after repeated shaking, dissolved *without* precipitation of sulphur, but with an increase of temperature from 18° to about 50°. A very small precipitate of sulphur separated after the lapse of two or three days.

The mixture was kept for a week, and then concentrated on the water-bath until all the sulphurous acid was gone. To remove the larger portion of hydric chloride, lead carbonate was now added, and the filtrate from the lead chloride freed from lead in solution by the careful addition of hydric sulphate. The filtrate of the lead sulphate was concentrated to the sp. gr. 1·285. At this state of concentration, it measured 26·5 c.c. A qualitative examination of the liquid revealed the presence of hydric pentathionate and a trace of trithionate. A strong solution of potassic acetate was added, and the mixture allowed to evaporate in a current of ordinary air. A crystalline cake which formed in the course of the two following days, was freed from adhering mother-liquor by pressure between folds of filtering-paper; 11·5 grams of solid matter so obtained dissolved in 15 c.c. of water and 0·3 c.c. of hydric sulphate, and left only a few milligrams of sulphur as residue.

The filtered solution on spontaneous evaporation yielded 7·2 grams of crystals, too small for mechanical separation. They were therefore redissolved in another similar quantity of acidulated water, and the solution left to concentrate at ordinary temperatures. This time a crop of fine large crystals of potassic pentathionate and tetrathionate were obtained. Both descriptions of crystals could easily be separated.

Analysis of the Pentathionic Crystals.

0·52 gram dried over hydric sulphate left after ignition 0·252 gram of potassic sulphate.

In 100 parts	Found.	Theory.
Potassium	21·72	21·60

The substance gave the reactions of a pure pentathionate.

Analysis of Potassic Tetrathionate.

0·6934 gram dried over hydric sulphate gave after ignition 0·396 gram of potassic sulphate.

In 100 parts	Found.	Theory.
Potassium	25·61	25·82

The reactions likewise agreed with those of a tetrathionate.

The polythionic acids have been formed in this experiment by the action of sulphurous acid on one of the products of decomposition of sulphurous chloride and water, viz., hydric thiosulphate, and I believe whenever nascent sulphur and sulphurous acid meet under favourable conditions polythionic acids will be formed. If so, then hydric pentathionate ought to result from the decomposition of hydric thiosulphate, $H_2S_2O_3$, in water.

25 grams of baric thiosulphate were digested with 9·1 grams of hydric sulphate diluted with five times its weight of water. The filtrate from the baric sulphate, after concentration on the water-bath, gave a liquid which comported itself with potassic hydroxide, ammonia-silver nitrate, and mercurous nitrate respectively, like a solution of hydric pentathionate. But a considerable portion of the hydric thiosulphate had decomposed into water, sulphur, and sulphurous acid.

Will ordinary sulphur produce polythionic acids with sulphurous acid?

A quantity of flowers of sulphur was washed for a long time, first with cold, afterwards with boiling water, until the wash-water did not change blue litmus paper. Some of the washed sulphur was placed on blue litmus paper, and left on it for some time. The colour did not change. 10 grams of the washed and dried flowers of sulphur were sealed with 36 c.c. of concentrated sulphurous acid in a glass tube, and a second tube charged with the same volume of acid without sulphur.

The two tubes remained for five days at common temperatures, and were then heated for several hours on a water-bath to 60—80°. This treatment did not appear to have effected any change in either of the tubes. Both were now opened, their contents transferred to evaporating dishes, and warmed on water-baths until all the sulphurous acid had volatilised.

I observed on this occasion that the acid escaped from the dish containing sulphur at a much slower rate than it did from the other. Both liquids were finally concentrated to one-fifth of their original volume.

Examination of the Liquid left by the Pure Sulphurous Acid.

The blue colour of litmus paper was changed to red; baric chloride gave a white precipitate insoluble in hydric chloride, and mercurous nitrate a white precipitate of mercurous sulphate. Addition of ammonia-silver nitrate produced no change, and cupric sulphate gave no reaction at 100°. But silver nitrate caused a very slight flocculent precipitate of a very pale brownish colour. Hence hydric sulphate is present and polythionic acids are absent.

Examination of the Liquid left by Sulphurous Acid and Sulphur.

Baric chloride indicated the presence of hydric sulphate, and mercurous nitrate gave a precipitate of mercurous sulphate which was coloured slightly yellow. Ammonia-silver nitrate produced a *very slight* brownish coloration, and a few brown gelatinous flakes made their appearance after some time. Silver nitrate caused a *very small* brown precipitate.

From these reactions it seems to follow that sulphurous acid and flowers of sulphur form under the conditions described an infinitesimal quantity of hydric pentathionate. This result is, however, of a very doubtful nature. Only one reaction, the one with the silver solution, can be advanced in its favour, and as the number of substances which reduce silver solutions is very great, no certain conclusion can be drawn from the experiment. Commercial flowers of sulphur is a very impure substance. It contains sulphates of various descriptions, hydric, calcic, aluminic, and iron sulphates were found in the wash-water. The latter gave with silver nitrate a precipitate which gradually became *black*. Some of the wash-water was first concentrated on the water-bath, and then evaporated to dryness on a piece of platinum foil. It left a considerable residue, which at a higher temperature evolved hydric sulphate, and at a red heat assumed a *transient* black colour as if an organic substance were present.

On the whole, the experiment with flowers of sulphur and sulphurous acid is of a negative nature, and we are only certain that nascent sulphur with water and sulphurous acid produces polythionic acids.

Explanation of the Formation of the Constituents of Wackenroder's Solution.

We are now able to explain the formation of the constituents of Wackenroder's solution from the original materials, sulphuretted hydrogen, sulphurous acid, and water. Hydric sulphide and sulphurous acid in the presence of water react immediately with separation of sulphur (p. 336). It appears that hydric pentathionate is not the direct product of this reaction (p. 338), at all events the greater part of it is slowly formed, when a solution of sulphurous acid, only partially decomposed by sulphuretted hydrogen, is kept for some days (p. 339). A current of sulphuretted hydrogen passed through 120 c.c. of sulphurous acid without interruption until all the acid is decomposed, causes the formation of a small quantity of hydric pentathionate (p. 342). If the current of hydric sulphide is stopped after the decomposition of about half of the sulphurous acid and the liquid is now allowed to remain at rest for two days, and

after the lapse of this time sulphuretted hydrogen is again passed until the operation is completed, a larger quantity of hydric pentathionate is produced.

But the best yield of hydric pentathionate is obtained when the passage of the hydric sulphide is interrupted five or six times, each time for from 36 to 48 hours, during the course of the entire operation (p. 281).

The following table contains an outline of the experimental results :—

Time required for the complete decomposition of sulphurous acid by sulphuretted hydrogen.	Ratio of the weights of the salts obtained.	
	Potassic tetrathionate.	Potassic pentathionate.
I. 3 to 4 hours for 120 c.c. in one operation	6	1
II. Sulphuretted hydrogen passed twice, each time 1½ hours on separate days. Quantity 120 c.c.	6	2
III. Sulphuretted hydrogen passed 8 times, each time 2 hours on separate days. Quantity 480 c.c.	6	6

The quantity of tetrathionate appears to be proportionally the same in all experiments, and quite independent of the time of preparation. From this I conclude that hydric tetrathionate is a direct product of the reaction of sulphuretted hydrogen on sulphurous acid, and is formed by combination as represented by the equation—

$$3SO_2 + H_2S = H_2S_4O_6.$$

If hydric sulphide and sulphurous acid, respectively, had no action on hydric tetrathionate then the latter would be the sole product of the reaction. But as both decompose the tetrathionate, an unusual complexity of reactions is the result.

As long as the sulphurous acid is in great excess, as in the beginning of the operation, most of the sulphuretted hydrogen reacts with the sulphurous acid, and we may at this stage disregard the reaction between the tetrathionate and sulphide. The two substances, hydric sulphide and sulphurous acid, meeting in aqueous solution in the proportions of the above equation, and in their positions of reaction, combine and form hydric tetrathionate. But the hydric tetrathionate molecules and free sulphurous acid produce hydric trithionate, and thiosulphuric acid, S_2O_2 (pp. 333 and 334). This reaction, however, is

very slow, and of a reciprocal nature. In consequence it is only partial, and as thiosulphuric acid can transfer sulphur to hydric tetrathionate, and so cause the formation of hydric pentathionate, the solution will now contain—

Free sulphurous acid,
Thiosulphuric acid,
Hydric trithionate,
Hydric tetrathionate, and
Hydric pentathionate.

If now sulphuretted hydrogen were passed in until all sulphurous acid had disappeared, and if no other reactions took place, then hydric tri-, tetra-, and penta-thionates would be the products. And for every molecule of hydric pentathionate a molecule of hydric trithionate would be present. This result is modified by the reaction we have so far disregarded, viz., by the decomposition of the hydric tetrathionate by sulphuretted hydrogen into water and sulphur; one part of the sulphur so set free combines in *statu nascendi*, with hydric trithionate to form hydric tetrathionate, and with tetrathionate to form pentathionate, and with the latter to form hexathionate. The quantitative relations are such that at the moment when all the sulphurous acid has disappeared, all the hydric trithionate has also been reconverted into tetrathionate. Another part of the sulphur produced by the action of hydric sulphide on hydric tetrathionate remains in solution as colloïdal sulphur—δ-sulphur—and the remaining quantity falls down as a precipitate or remains in suspension.

If then the three reactions—the formation of hydric tetrathionate and its decomposition by sulphuretted hydrogen and sulphurous acid, respectively—are taken into consideration, we should have as final products of the action of sulphuretted hydrogen on an aqueous solution of sulphurous acid: sulphur as a precipitate, sulphur in suspension, sulphur in solution, and hydric tetra-, penta-, and hexathionates.

This is the condition of the Wackenroder solution, the preparation of which has been described on p. 340. Hydric tetrathionate is the chief product.

But if the passage of the sulphuretted hydrogen through the solution of sulphurous acid is conducted with interruptions of several hours' duration, then the condensation of thiosulphuric acid into pentathionic acid with formation of hydric pentathionate (p. 281) takes place, and the quantity of the pentathionate becomes in consequence five or six times greater than before. And if sulphuretted hydrogen is passed through a Wackenroder solution after all the sulphurous acid has disappeared, and until it ceases to act on the polythionic

acids present, water and sulphur will be the final products of decomposition.

The polythionic acids are then intermediate products of the reaction of sulphuretted hydrogen with an aqueous solution of sulphurous acid, and the equation—

$$SO_2 + 2H_2S = S_3 + 2H_2O,$$

given by the text-books is correct for the final products.

C. *On the Formulæ of the Polythionates.*

We will now attempt to represent the constitution of the polythionates by rational formulæ, derived from the chemical facts described in this and the papers of other authors. In some of the best of our text-books,* the formula—

$$S_3(SO_2OH)_2,$$

is given for hydric pentathionate, and it is stated that baric pentathionate is formed from baric thiosulphate and sulphuric chloride according to the equation—

$$2\left[SO_2\begin{cases}O\\S\end{cases}>Ba\right] + SCl_2 = BaS_5O_6 + BaCl_2.$$

These formulæ we will trace to their original sources.

Bloomstrand (*Chemie der Jetzzeit*, 158) appears to have been the first chemist who represented hydric pentathionate by the formula $S_3(SO_2OH)_2$, and Mendeléeff (*Ber.*, **3**, 870) after him adopted the same expression.

The latter believes that several unknown compounds of sulphur and hydrogen can exist, H_2S_3, H_2S_4, H_2S_5, all derived from sulphuretted hydrogen by replacing an atom of hydrogen by the residue HS. If now in the compounds of sulphur and hydrogen, H_2S, H_2S_2, and H_2S_3, the two hydrogen-atoms are replaced by the radical of hydric sulphate, SO_3,H, the formulæ of hydric tri-, tetra-, and penta-thionate are obtained.

$$S\begin{cases}H\\H\end{cases} + \begin{matrix}OH\cdot SO_2\cdot OH\\OH\cdot SO_2\cdot OH\end{matrix} = S<\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix} + 2H_2O.$$

Hydric trithionate.

$$S_2\begin{cases}H\\H\end{cases} + \begin{matrix}OH\cdot SO_2\cdot OH\\OH\cdot SO_2\cdot OH\end{matrix} = S_2<\begin{matrix}SO_3\cdot OH\\SO_2\cdot OH\end{matrix} + 2H_2O.$$

Hydric tetrathionate.

* Kolbe, H, *A Short Text-Book of Chemistry*, translated by Prof. Humpidge. London, 1884, p. 171. Richter, *Lehrbuch*, 1881, p. 222; *Roscoe and Schorlemmer*, 1, p. 354.

$$S_3\begin{cases}H\\H\end{cases} + \begin{matrix}OH\cdot SO_2\cdot OH\\OH\cdot SO_2\cdot OH\end{matrix} = S_3<\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix} + 2H_2O.$$

Hydric pentathionate.

Mendeléeff shows that the hydrogen salts of the polythionic acids agree in several respects with the sulphonic acids, and that his formulæ indicate how to prepare the former in a rational manner. As an example, he mentions that sulphurous chloride and dipotassic sulphite ought to give potassic tetrathionate :—

$$S_2Cl_2 + \begin{matrix}K\cdot SO_3\cdot K\\K\cdot SO_3\cdot K\end{matrix} = S_2<\begin{matrix}SO_3K\\SO_3K\end{matrix} + 2KCl.$$

Mendeléeff has not, as far as I know, made this experiment, or tested his theoretical conceptions in other ways. This work has been carried out by W. Spring (*Ber.*, **6**, 1108), who did not realise the last equation, but obtained instead of potassic tetrathionate trithionate and some potassic thiosulphate. Sulphuric chloride and dipotassic sulphite gave likewise potassic trithionate and also potassic chloride. The equation—

$$SCl_2 + 2KSO_3K = 2KCl + S(SO_3K)_2,$$

is given in explanation of the reaction.

But Spring did not use sulphuric chloride and dipotassic sulphite only, he also had water present. And if the water is taken into consideration, then a very different explanation may be given of his results.

Sulphuric chloride, SCl_2, and water produce sulphurous acid, hydric chloride, and sulphur. Hydric chloride decomposes dipotassic sulphite into potassic chloride, water, and sulphurous acid. If the reacting substances are taken in quantities as required by the equation half the dipotassic sulphite remains undecomposed. Dipotassic sulphite and sulphur form potassic thiosulphate.

The latter and sulphurous acid produce, as is well known, potassic trithionate, and as has been shown in this paper some potassic tetrathionate and pentathionate. Consequently, the results of Spring's experiments can be explained by well-known facts, and as they can be explained in more than one way, it follows that his experiments cannot throw any light on the constitution of the polythionates, and the same remarks may be made with regard to the experiment with baric thiosulphate.

Spring mixed this salt with some water and then added sulphurous chloride, S_2Cl_2.

After precipitation of the dissolved barium by an excess of hydric sulphate and the excess of hydric sulphate by baryta-water, he

obtained a liquid which gave "all the reactions of pentathionic acid." Therefore the formula of this acid is—

$$S_3<\begin{matrix}SO_3H\\SO_3H\end{matrix}.$$

The experiment teaches *nothing* about the constitution of pentathionic acid. Sulphurous chloride and water alone without the assistance of baric thiosulphate will furnish a liquid exhibiting the reactions of hydric pentathionate, or baric thiosulphate and dilute hydric sulphate without sulphurous chloride will do the same.

The formula $S_3<\begin{matrix}SO_3H\\SO_3H\end{matrix}$ is therefore a purely hypothetical conception, and it is to be regretted that on the evidence described, it has been admitted in books intended for beginners.

The metallic salts of sulphurous acid are, according to Strecker's reaction (*Annalen*, **148**, 90—119), constituted as follows :—

$$Ag{\cdot}SO_2{\cdot}O{\cdot}Ag,$$

viz., one atom of metal, silver in this case, is *directly* combined with sulphur.

Bunte's (*Ber.*, **7** (1874), 646) experiments confirm Odling's (*Chem. Soc. J.*, **22**, 255) formula for the thiosulphates. Sodic ethylic thiosulphate and hydric chloride produce mercaptan, sodic chloride, and hydric sulphate—

$$C_2H_5{\cdot}S{\cdot}SO_2{\cdot}ONa + H_2O + HCl = C_2H_5SH + NaCl + H_2SO_4,$$

hence the ethyl of the thiosulphate is in *direct* combination with sulphur. The behaviour of the thiosulphate with mercuric chloride agrees with this conclusion. The salts of potassium have a similar constitution, hence—

Dipotassic sulphite, $K{\cdot}SO_2{\cdot}OK$,
Potassic thiosulphate, $K{\cdot}S{\cdot}SO_2OK$.

Dipotassic sulphite combines directly with sulphur to produce the thiosulphate. This sulphur, therefore, joins the group KSO_3 of dipotassic sulphite. On the other hand, some thiosulphates, for example, the calcium salt, easily lose sulphur and become sulphite. Hence this second atom of sulphur of thiosulphates is held by a feeble force only.

Potassic thiosulphate and iodine produce potassic tetrathionate and potassic iodide. Three formulæ are probable for the tetrathionate :—

$$\text{I.}\quad \begin{matrix}KS{\cdot}SO_2{\cdot}OK\\KS{\cdot}SO_2{\cdot}OK\end{matrix} + I_2 = \begin{matrix}S{\cdot}SO_2{\cdot}OK\\|\\S{\cdot}SO_2{\cdot}OK\end{matrix} + 2(KI).$$

$$\text{II.}\quad \begin{matrix}KS\cdot SO_2\cdot OK\\ KS\cdot SO_2\cdot OK\end{matrix} + I_2 = \begin{matrix}KS\cdot SO_2\cdot O\\ |\\ KS\cdot SO_2\cdot O\end{matrix} + 2(KI).$$

$$\text{III.}\quad \begin{matrix}KS\cdot SO_2\cdot OK\\ KO\cdot SO_2\cdot SK\end{matrix} + I_2 = \begin{matrix}KS\cdot SO_2O\\ |\\ KO\cdot SO_2S\end{matrix} + 2(KI).$$

Potassic tetrathionate can lose one atom of sulphur and become trithionate; hence we have one of the three following formulæ for the last-named salt:—

$$\text{IV.}\quad S<\begin{matrix}SO_2\cdot OK\\ SO_2\cdot OK\end{matrix};\quad \text{V.}\quad \begin{matrix}KSO_2\cdot O\\ |\\ KS\cdot SO_2\cdot O\end{matrix}\quad \text{VI.}\quad \begin{matrix}K\cdot SO_2O\\ |\\ KO\cdot SO_2S\end{matrix}.$$

Now potassic trithionate can combine with sulphur in *statu nascendi* as dipotassic sulphite does.

The power to take up sulphur belongs in the case of the last-named salt to the atomic group KSO_2 (p. 353), and we shall be justified in attributing, in the case of the trithionate, the same property to the same cause, viz., to assume in the trithionate the presence of the group KSO_3. This assumption is also supported by the fact that potassic trithionate is a derivative of potassic hydric sulphite and sulphur. Hence the formula IV must be eliminated, because it does not contain the atomic group KSO_3, and there remain the formulæ V and VI for the trithionate.

Our choice is guided by the following considerations:—Two of the sulphur-atoms of the potassic pentathionate occupy positions in the molecule essentially different from those of the other three. These two atoms of sulphur can, successively or together, be removed, and the residue of the molecule can exist by itself, or can reunite with sulphur, and reproduce pentathionate.

The trithionate behaves with regard to sulphur like an element. But if an atom of sulphur is removed from potassic trithionate, then the residue $K_2S_2O_6$ decomposes at the same time into potassic sulphate and sulphurous acid, and from these materials the original salts ($K_2S_3O_6$, $K_2S_5O_6$) cannot be obtained by direct combination. From this it follows that one of the three sulphur atoms of potassic trithionate holds the proximate constituents of the salt in chemical combination, viz., the existence of the salt as a polythionate is dependent on this sulphur-atom. This condition is satisfied by formula VI, but not by formula V.

We support this conclusion by the following experiments and considerations:—

If potassic pentathionate had the constitution—

$$S_3(SO_2\cdot OK)_2,$$

bromine-water would decompose the salt according to the equation—

$$S_3SO_2{\cdot}OK_2 + Br_2 + 2H_2O = S_3 + 2K\dot{B}r + 2H_2SO_4.$$

I. 1·4089 grams of potassic pentathionate were dissolved in water, and mixed by degrees with bromine water containing 0·624 gram or 1 mol. of bromine. Every drop of bromine-water caused turbidity, which disappeared again on stirring the mixture with a glass rod. But it remained thick after a certain quantity of bromine had been added. A precipitate of sulphur fell down. This was of a soft, plastic nature, and was collected on a weighed filter. Its weight was found to be = 0·075 gram, but on account of its soft nature it could not be powdered in a mortar, and could not be entirely freed from potassium salts by washing. Heated on platinum foil, it left some residue. The filtrate from the sulphur precipitate contained much potassic pentathionate and hydric or potassic sulphate. It was slightly opalescent, and on standing deposited a thin membrane of sulphur on the side of the beaker. Probably some of the sulphur separated by bromine had combined with undecomposed pentathionate to form hexathionate, and the spontaneous decomposition of the latter caused the deposition of the sulphur membrane. Sodic chloride caused no precipitate in the filtrate.

II. 0·561 gram potassic pentathionate was mixed in aqueous solution by degrees with 0·497 gram of bromine (2 mols.). The sulphur precipitate weighed, after washing with diluted ammonia and drying over hydric sulphate, 0·0635 gram. The filtrate contained, besides undecomposed thionate, sulphates.

III. 1·0965 grams of potassic pentathionate were mixed in aqueous solution with 1·948 gram of bromine (4 mols.). The precipitated sulphur was at first soft, but soon became hard and brittle. It was powdered in an agate mortar, washed with dilute ammonia, and dried over hydric sulphate. Its weight was 0·206 gram. *The filtrate was no longer acted on by bromine-water.* All potassic pentathionate had been decomposed.

Baric chloride added to the filtrate gave a precipitate of baric sulphate weighing 2·034 grams. Hence 1·0965 gram of potassic pentathionate gave with bromine-water 0·206 gram of sulphur as a precipitate, and 0·279 gram in the form of baric sulphate.

In 100 parts—

	Found.	Theory.
Sulphur.....	44·31	44·32

Therefore 4 mols. of bromine had precipitated from 1 mol. of potassic pentathionate 2·13 atoms of sulphur, and oxidised to sulphuric acid 2·87 atoms.

I.	One mol. of potassic pentathionate, $K_2S_5O_6$.....	+	1 mol. of bromine	gave 0·6	atom of sulphur.
II.	Ditto	+	2 mols.	„ 1·27	„
III.	Ditto	+	4 mols.	„ 2·13	„

The sulphur in I and II, on account of its physical properties, could not be obtained quite pure by washing; hence it has been found too high.

From these experiments I conclude that the decomposition of potassic pentathionate by bromine-water takes place according to the equation—

$$2K_2S_5O_6,3H_2O + 8Br_2 + 9H_2O = 4KBr + 4S + 6H_2SO_4 + 12HBr,$$

and that if less bromine be taken than is required by this equation, a proportionate quantity of pentathionate remains undecomposed.

Two atoms of the sulphur of a molecule of potassic pentathionate, $K_2S_5O_6$, are precipitated as such, and three are oxidised to sulphuric acid. The conclusion is that the three oxidisable atoms of sulphur are already in the molecule of pentathionate in combination with oxygen, and are so in the trithionate resulting from the decomposition of the pentathionate. As the formula V does not fulfil these conditions we must eliminate it, and we have then only one formula, VI, left for potassic trithionate, and this formula agrees with the properties of the salt. We find then the following formulæ for the potassic polythionates:—

$$\begin{matrix} K\cdot SO_2\cdot O \\ \quad | \\ KO\cdot SO_2\cdot S \end{matrix}$$ Potassic trithionate.

$$\begin{matrix} KS\cdot SO_2\cdot O \\ \quad | \\ KO\cdot SO_2\cdot S \end{matrix}$$ Potassic tetrathionate.

$$\begin{matrix} KS_2\cdot SO_2O \\ \quad | \\ KO\cdot SO_2\cdot S \end{matrix}$$ Potassic pentathionate.

$$\begin{matrix} KS_3\cdot SO_2\cdot O \\ \quad | \\ KO\cdot SO_2\cdot S \end{matrix}$$ Potassic hexathionate.

According to these formulæ, potassic trithionate contains the group $K\cdot SO_2$, in which the potassium is in direct combination with the sulphur.

Potassic sulphide, K_2S, can combine with two, three, or more atoms of sulphur, and this property of potassic sulphide is not lost in

the combination $K \cdot SO_2$. The hydrogen salt of tetrathionic acid contains, according to this theory, the radicals HO and HS, and that of pentathionic acid the radicals HO and HS_2, and hydric hexathionate HO and HS_3. The hydrogen of these radicals is replaceable by metals. HS_2 also occurs in persulphide of hydrogen, and, like this compound, potassic pentathionate is immediately decomposed by alkalis and rendered more stable by acids. Water also causes both substances to decompose in the same manner. *Moist* persulphide of hydrogen produces sulphuretted hydrogen and sulphur, a solution of potassic pentathionate, potassic tetrathionate and sulphur. Groups of the same constitution as HS_2 and KS_2 confer similar properties on the compounds in which they occur.

Royal Naval College, Greenwich,
December, 1887.

XXVI.—*Note on the Density of Cerium Sulphate Solutions.*

By B. Brauner, Ph.D., F.C.S., late Fellow of Owens College.

(Communication from the Laboratory of the Bohemian University, Prague.)

Since the publication of Mendeléeff's paper on the Density of Salt Solutions (*Russ. Chem. Soc. Journ.*, 1884, 184, in which this eminent chemist shows that the density of solutions regularly increases with the molecular weight of the salts dissolved) and especially since the publication of the same author's important work on Solutions,* the interest of chemists has been, more than ever, directed to this subject; every new exact determination, therefore, may be regarded as useful material for a further study of this important subject.

In the case of the rare earth metals, not a single solution has as yet been studied from this point of view, partly on account of the rarity

* Д. Менделѣевъ. Изслѣдованіе водныхъ растворовъ по удѣльному вѣсу. С.-Петербургъ, 1887 (D. Mendeléeff. "Research on Aqueous Solutions with regard to their Density," St. Petersburg, 1887, 21, and 520 pages large 8vo.). In this important work, which, on account of its theoretical and practical value, ought to be translated into a Western-European language, the whole of the material relating to the density of aqueous solutions is collected and analysed with an originality peculiar to the great Russian chemist.

of the material, partly because only a very few of the rare earths can be regarded as homogeneous bodies.

For the present investigation, cerium (cerous) sulphate was used, which served me for the determination of the atomic weight of cerium (Trans., 1885, 879); cerium sulphate, as regards its solubility in water exhibits two peculiarities by which it is distinguished from the majority of salts. It is more soluble in cold than in warm water, and the anhydrous salt is not only more soluble, but far more easily soluble in water, than the hydrated salt.

Many chemists assume that each of these salts is dissolved in water as such, and that the solubility at a higher temperature decreases, because on heating the cold saturated solution of the anhydride, hydrates of the salt which cannot exist in solution at that high temperature are formed and deposited.

The question, whether a solution of an anhydrous salt is identical with that of the hydrated salt, has been discussed of late especially by English chemists, and therefore in the present case I tried to determine whether there was any difference observable between solutions of the anhydrous and hydrated cerium sulphates of equal concentration.

The following experiments show the unequal solubilities of the anhydrous and the hydrated salts.

If anhydrous cerium sulphate is added to water at 0—3°, little by little, with continuous stirring, it dissolves quickly and completely until 60 parts of anhydrous sulphate have been used for 100 parts of water. If more of the salt is added, it is not only converted into crystals of the hydrate but crystals of the hydrate are also gradually deposited from the solution, this being accompanied by development of heat. When the temperature of the liquid (and salt) has risen to 15°, it becomes converted into a kind of crystalline paste. On stirring this for some time at 15°, until no further separation of crystals takes place, and then separating the liquid from the solid portions, a solution is obtained containing 27·88 parts of the anhydrous sulphate to 100 parts of water.

If 31·62 parts of the anhydride be dissolved in 100 parts of water at 0—3°, no salt separates out from the solution on raising its temperature to 15°. This is, however, the maximum of concentration of a solution whose density can be determined in the usual way, for after standing for some time at 15° crystals of a hydrate begin to separate out in the picnometer. When the solution has been standing for some days exposed to the air at 15—18° in an open vessel, so that spontaneous evaporation occurs, a great part of the salt crystallises out, and a solution remains containing 17·69 parts of the anhydride to 100 parts of water.

How difficult it is to attain the final point of saturation, without starting with a supersaturated solution, may be seen from the following. Anhydrous sulphate, 14·56 parts, was dissolved in 100 parts water at 3°. After standing for a few days exposed to the air, numerous crystals of a hydrate separated, but the saturated solution contained only 15·59 parts of anhydride to 100 of water. Crystals of the hydrate $Ce_2(SO_4)_3 + 8H_2O$, were stirred from time to time with water at 15° during two days in such proportion that a great part of the salt remained undissolved; in this case, only 17·52 parts (anhydrous salt) were dissolved by 100 water. On one occasion, a solution of 19·80 parts of the anhydride in 100 water was obtained on concentration by spontaneous evaporation, but on trying to obtain such a saturated solution of the hydrate once more in the same way, solutions were obtained, containing, after two days, 11·66 parts, and after five days only 12·24 parts in 100 water.

From this it will be seen, that, on saturating water with cerium sulphate at the mean temperature of 15—18°, solutions may be obtained containing from 12·24 to 31·62 parts of salt in 100 water; it is, however, difficult to determine the point at which "saturation" ceases and "supersaturation" begins.

For the determination of the density of the solutions, two Thorpe picnometers of 18·9 c.c. (*a*) and 22·5 c.c. (*b*) capacity were used. In the middle of the narrow neck, two fine lines 1 mm. distant were engraved, and the volume of each of these intervals was determined by putting into the vessel, full of water, a drop of mercury of a known weight (Mendeléeff). This volume was found to be for *a* 0·0054 and for *b* 0·0042 c.c. As one-tenth of that interval can be measured by optical means, the corresponding sp. gr. can be estimated to within about $\pm 0{\cdot}00002$.

The temperature was determined by means of a normal Geissler thermometer, showing distinctly 0·01°, the zero point of which was corrected several times during the investigation. All determinations were made at 15°; and in order to keep this temperature constant for a sufficient length of time in the glass vessel (with flat sides) containing about 4 litres of water into which the picnometers were plunged, the temperature of the surrounding air was kept artificially at 15·5—15·6°.

The weights used were carefully corrected and the weight of the liquids and vessels reduced to a vacuum. By using the method of vibrations, the error does not exceed 0·1 mgrm., which makes the error $\pm$ 0·00001 in the density. For calculation of the sp. gr. 0·999159 was taken as the mean density of water at 15°, water at 4° = 1. The air was pumped out of the solutions before weighing, but this could not be carried too far in the case of the more concentrated solutions.

After each determination, the contents of the picnometer was transferred to a weighed platinum crucible, and this was weighed in a thin glass weighing bottle, so as to prevent any loss which might be caused by evaporation. The solution was then carefully evaporated on the water-bath, and the anhydrous salt obtained by heating the crucible at 440° in the sulphur-bath described in the paper quoted above. The experimental error caused by inexact determination of the amount of salt in solution has the greatest influence on the final result, for a difference of $\pm 0{\cdot}005$ part of salt in 100 parts of water makes as much as $\pm 0{\cdot}00005$ in the density.

The first series of experiments was made with solutions of the anhydrous sulphate, the second series with solutions of the hydrated salt of nearly equal concentration; these were prepared afresh for each experiment by synthesis. The first column of the tables A and B below shows the quantity of anhydrous salt contained in solution for 100 parts of water present (not the percentage), the second the

A. *Solutions of the Anhydrous Sulphate,* $Ce_2(SO_4)_3$, *at* 15°/4°.

$\frac{x}{100}$.	$\frac{1}{y}$.	Density found.	Density mean.	Calculated.	Difference.
3·17	995·9	1·030026 1·030071	1·03005 ±0·00002	1·03006	−0·00001
6·11	516·6	1·058082 1·058151	1·05812 ±0·00004	1·05795	+0·00017
8·46	373·4	1·080026 1·079983	1·08000 ±0·00002	1·08003	−0·00003
9·61	328·7	1·090810 1·090880	1·09085 ±0·00004	1·09077	+0·00008
10·55	299·5	1·099418 1·099362	1·09939 ±0·00003	1·09952	−0·00013
12·66	249·5	1·119153 1·119169 1·119171 1·119196	1·11917 ±0·00002	1·11905	+0·00012
14·56	216·9	1·136646	1·13665	1·13651	+0·00004
15·64	203·6	1·146212 1·146247	1·14623 ±0·00002	1·14637	−0·00014
21·19	149·1	1·196426 1·196367	1·19640 ±0·00003	1·19649	−0·00009
31·62	99·9	1·28777	1·28778	1·28788	−0·00010

number of molecules of H_2O holding 1 mol. of the respective salts (anhydrous and hydrated) in solution, the third the density found, the fourth the mean numbers, the fifth the numbers calculated by the interpolation formulæ given below, the sixth the differences between the numbers calculated and found.

B. *Solutions of the Hydrated Sulphate*, $Ce_2(SO_4)_3 + 8H_2O$.

$\frac{x}{100}$.	$\frac{1}{y}$.	Density found.	Density mean.	Calculated.	Difference.
3·18	994·2	1·030060 1·030068 1·030075 1·030106	1·03008 ±0·00002	1·03015	−0·00007
6·31	500·3	1·059961 1·059957	1·05996 ±0·00000	1·05991	+0·00005
8·35	378·4	1·079062 1·079130	1·07910 ±0·00003	1·07902	+0·00008
8·48	372·3	1·080337 1·080282	1·08031 ±0·00003	1·08029	+0·00002
10·53	299·9	1·099292 1·099273	1·09928 ±0·00001	1·09936	−0·00008
10·56	299·2	1·099606 1·099564	1·09959 ±0·00002	1·09960	−0·00001
11·66	273·2	1·109857 1·109883	1·10987 ±0·00001	1·10981	+0·00006
12·24	257·9	1·115294 1·115300	1·11530 ±0·00000	1·11521	+0·00009
14·52	217·6	1·136180	1·13618	1·13605	+0·00013

In order to see whether the densities of the solutions of the anhydrous salt are identical with those of the hydrate of equal concentration, the densities for equal concentration had to be calculated. Dr. A. Seydler, Professor of Natural Philosophy in our University, has kindly calculated, by a complicated formula involving the use of the method of least squares, the equations for parabolas showing the dependence of the density on the concentration in both series of experiments, but as the equations were calculated only from the data obtained by me, without regard to the fact that water at 15° has a density of 0·99916, the corresponding values in the equations had to be extrapolated, which makes them somewhat uncertain (0·99966 and

0·99964 instead of 0·99916) Other methods of calculation, however gave no better results. The equations are (d = density at 15°, x = salt for 100 parts water):

(A.) For the anhydride: $d = 0{\cdot}999665 + 0{\cdot}0096401x - 0{\cdot}0000166x^2$.
(B.) For the hydrate: $d = 0{\cdot}999636 + 0{\cdot}0096646x - 0{\cdot}00001839x^2$.

The values calculated by the aid of these formulæ for 2 to 14 parts of salt in 100 water (14 being the maximum of concentration of the solution of the hydrate) are given in the following table:—

$\frac{x}{100}$.	Density of anhydride solution.	Density of hydrate solution.	Difference.
0	0·99967	0·99964	−0·00003
2	1·01888	1·01889	+0·00001
4	1·03796	1·03800	+0·00004
6	1·05691	1·05696	+0·00005
8	1·07572	1·07578	+0·00006
10	1·09441	1·09444	+0·00003
12	1·11296	1·11296	0·00000
14	1·13137	1·13134	−0·00003

From a comparison of both series, it follows—

1. That the densities of solutions of anhydrous cerium sulphate are *identical* with the densities of the solutions of the hydrated salt.

2. That the differences in both series fall entirely within the unavoidable experimental errors, for the differences never exceed those between the numbers found and calculated, as is seen from Tables A and B.

Finally, it should be mentioned, that, if solutions of the hydrate and those of the anhydride of equal concentration, be evaporated in vessels of equal size and material on the same water-bath, those of the anhydride will show an inclination to deposit monoclinic prisms of the salt, $Ce_2(SO_4) + 5H_2O$, whereas solutions of the hydrate + $8H_2O$, are more inclined to deposit rhombic octahedrons of the salt, $Ce_2(SO_4)_3 + 8H_2O$. This difference in behaviour of the two solutions holds good only for those concentrations in which the salt begins to be deposited, not on merely *heating the solutions*, but only after some water had evaporated. I cannot say definitely whether this may not

be due partly to chance; that it is really the case, however, is seen from the following analyses:—

(*a.*) *Evaporation of a Solution of the Anhydrous Salt.*

The salt, $Ce_2(SO_4)_3 + 5H_2O$, is stable at 100°.

	Grams.	Water in per cent.	Calculated for $Ce_2(SO_4)_3 + 5H_2O$.
Weight of salt—			
(*α.*) Directly after evaporation at 100°	1·4677	14·51	13·66
After drying at 100° for 5 hours.....	1·4474	13·31	
After drying at 100° for 10 hours.....	1·4458	13·19	
After drying at 100° for 15 hours.....	1·4445	13·14	
Weight of anhydrous salt (440°).....	1·2547		
(*β.*) Salt at 100°	1·1828	13·72	
Salt at 440°	1·0204		
(*γ.*) Salt at 100°	1·2244	13·62	
	1·0577		

(*b.*) *Evaporation of a Solution of the Hydrated Salt.*

The salt, $Ce_2(SO_4)_3 + 8H_2O$, loses 4 mols. H_2O at 100°.

	Grams.	Water in per cent.	Hydrate.	Requires.
Weight of salt—				
(*α.*) After evaporation at 100°	1·4975	19·92	$8H_2O$	20·21
After drying 2 hours at 100°	1·3479	11·03	$4H_2O$	11·24
Anhydrous at 440°.....	1·1992			
(*β.*) Salt at 100°.....	1·3093	11·11	$4H_2O$	11·24
Salt at 440°.....	1·1639			

XXVII.—*A Gasometric Method of Determining Nitrous Acid.*

By Percy F. Frankland, Ph.D., B.Sc., F.I.C., Assoc. Royal School of Mines.

In the course of some experiments which I have been carrying on for some time past, it became necessary to determine the proportion of nitrous acid present in certain solutions containing both nitrates, nitrites, and ammonia, the problem being still further complicated by the presence of organic matter. The estimation of nitrous acid in such mixtures is usually effected colorimetrically by the well-known reactions of metaphenylenediamine, or of sulphanilic acid and naphthylamine hydrochloride, on an acidulated solution of the nitrite, the latter reaction being very much more delicate than the former. Both of these colorimetric methods are, however, only adapted for measuring very minute traces of nitrous acid, and were quite unsuitable for my purpose. I may, however, mention in passing that I have found the modification of the sulphanilic acid method introduced by Zambelli (Abstr., 1887, 533), very much to be preferred to either of the above well-known methods. Zambelli adds to the solution containing the nitrite a drop of a saturated solution of sulphanilic acid, then a drop of an aqueous solution of phenol, the mixture being then rendered alkaline with ammonia; the presence of nitrous acid is indicated by the appearance of a coloration, varying from faint yellow to intense reddish-yellow (like the colour of a strong solution of potassium dichromate), according to the quantity of the nitrous acid present. The author states that this method is capable of indicating the presence of 1 part of nitrous nitrogen in 40,000,000 parts of water. So that whilst its delicacy is extreme it has also the advantage, that the reagents employed are permanent in solution; the solutions of naphthylamine hydrochloride, and more especially of metaphenylenediamine becoming very rapidly discoloured on keeping. I, therefore, invariably adopt this method for qualitatively testing for nitrites, as well as for obtaining a relative estimate of the amount present in different solutions.

For the purposes of the experiments upon which I was engaged, however, it was necessary to have a method which should be capable of dealing with much larger quantities of nitrous acid than are suitable for colorimetric estimation. Owing to the presence of organic matter in the solutions in question, the ordinary method of determining nitrous acid by means of a standard solution of potassium permanganate was out of the question, and on this account a gaso-

metric method appeared to be the most suitable for the purpose, especially as only very small absolute quantities of the nitrite were available. Under these circumstances, the reaction between nitrous acid and urea naturally suggests itself as especially suitable, since the volume of nitrogen gas evolved is double that of the nitrogen in the nitrite, and the errors of experiment thus become divided by two. I have since found that this reaction had been utilised for the purpose of nitrous acid estimation by Longi (*Gazzetta*, **13**, 469—479), although his mode of operation is quite different from mine, and would not have been adapted to the determination of the small quantities of nitrous acid which I had at my disposal.

My preliminary experiments were made with a solution of sodium nitrite, standardised by means of potassium permanganate.

(1.) 20 c.c. of the standard solution of sodium nitrite are evaporated to dryness in a small beaker on the water-bath, to the residue is then added a large excess of crystallised urea (about 0·25 gram), about 2 c.c. of boiling water are then added from a wash-bottle to the mixture in the beaker, and in this the urea and nitrite rapidly dissolve; the solution is then carefully transferred to the cup of a tube similar to that used in the determination of nitric acid by the mercury-method, and as figured in the cut. This tube, which I employ, of the following dimensions (6″ long by $\frac{3}{4}$″ in diam. internal, the cup

being 1″ in depth) is filled with mercury, and stands in a mercury-trough. By carefully opening the tap, the liquid in the cup is

admitted into the tube. The beaker is now repeatedly rinsed with small quantities of boiling water, and the rinsings similarly transferred to the mercury-tube. An excess of dilute sulphuric acid (1 : 5) only amounting to a few c.c. in volume, is now poured into the cup, and admitted into the tube. A vigorous evolution of gas then commences, and continues for some five minutes. This gas consists of a mixture of nitrogen and carbonic anhydride. The decomposition in the cold with an excess of urea taking place according to Claus (*Ber.*, **4**, 140), as represented by the equation :—$2CO(NH_2)_2 + N_2O_3 = CO(NH_4O) + CO_2 + 2N_2$. After 15 minutes, when the decomposition may be taken to be complete, a strong solution (1 : 3) of pure caustic soda (free from nitrite) is added through the cup, and the mixture violently agitated until the carbonic anhydride is completely absorbed. The lower extremity of the tube is then firmly closed with the thumb, and the tube transferred to another mercury-trough, in which the gas and liquid are passed into the "laboratory-vessel" of an apparatus for the measurement of gases. The volume of nitrogen under known conditions of pressure and temperature is then ascertained, and from this the weight of nitrogen can be calculated. Thus in the experiment in question—

Volume of nitrogen = 13·79 c.c. Pressure = 255·5 mm. of mercury. Temperature = 18·9° C.
Weight of nitrogen from 10 c.c. of standard sodium nitrite solution = 0·0013615 gram.
Weight of nitrous nitrogen in ditto, determined by standard permanganate = 0·001346 gram.

(2.) 10 c.c. of the same sodium nitrite solution similarly treated, yielded—

Volume of nitrogen = 13·79 c.c. Pressure = 127·5 mm. of mercury. Temperature = 17·7° C.
Weight of nitrogen from 10 c.c. of standard sodium nitrite solution = 0·0013645 gram.

Thus the accordance of the nitrogen found with that calculated from the standardisation with permanganate is very close.

Experiments were made in order to determine whether the reaction between the urea and nitrite is really complete in 15 minutes, or whether a larger volume of nitrogen would be obtained if the time for the reaction was extended. Thus three portions, of 10 c.c. each, of a solution of sodium nitrite were evaporated in three small beakers, each of which was treated as above described; in the case of the first portion, the reaction with the urea was interrupted at the end of

15 minutes by the addition of the excess of caustic soda, whilst in the case of the second portion, the addition of the caustic soda was made after three hours, and with the third portion after 23 hours. The following results were obtained:—

	Reaction interrupted after	Volume of nitrogen.	Pressure in mm.	Temperature.	Weight of nitrogen from 10 c.c. of solution.
No. 1...	15 minutes	13·79 c.c.	252·7	13·2° C.	0·0013734 gram
„ 2...	3 hours	„	253·7	13·5 „	0·0013774 „
„ 3...	23 „	„	252·2	13·6 „	0·0013688 „

The above results show that the reaction is complete in 15 minutes, and that no more gas is evolved, even if the time is extended to 23 hours.

Comparison of Urea-method with Mercury-method of determining Nitrites.

Experiments were also made in order to compare the results of the urea-method with those obtained by the mercury-method, which does not discriminate between nitrous and nitric nitrogen. The same standard solution of sodium nitrite was employed for the purpose, with the following results:—

(1.) 20 c.c. of the solution of sodium nitrite were evaporated in a small beaker on the water-bath. The residue was then repeatedly extracted with very small quantities of hot water, and these successive extracts transferred to the mercury-tube as described above. The small beaker was then rinsed with strong sulphuric acid (free from nitrogen-compounds), and the rinsings, which amounted in volume to that of the aqueous extract, were also transferred to the mercury-tube. The mercury-tube was then closed at the bottom with the thumb of the right hand, and the tube violently shaken without, however, allowing the acid mixture in the tube to come in contact with the thumb. The evolution of nitric oxide commenced at once, and the pressure exerted by the liberation of the gas in the tube had to be relieved by withdrawing the thumb from the extremity of the tube when under mercury. The evolution of gas was complete in the course of a few minutes, and the gas was then transferred to the measuring apparatus as described before. In this case also, the volume of nitric oxide obtained is twice that of the nitrogen which it contains. Thus—

Volume of nitric oxide = 13·79 c.c. Pressure = 246·9 mm. of mercury. Temperature 16·3° C.

Weight of nitrogen from 10 c.c. of standard solution of sodium nitrite = 0·001328 gram.

(2.) 20 c.c. of the solution of sodium nitrite treated in a perfectly similar manner yielded—

Volume of nitric oxide = 13·79 c.c. Pressure = 256·2 mm. of mercury. Temperature = 16·6° C.
Weight of nitrogen from 10 c.c. of solution = 0·001376 gram.

(3.) 20 c.c. of the solution of sodium nitrite were evaporated to dryness in a small beaker, and the nitrous nitrogen determined by the urea-method. Thus—

Volume of nitrogen = 13·79 c.c. Pressure = 256·0 mm. of mercury. Temperature = 16·7° C.
Weight of nitrogen from 10 c.c. of solution = 0·001375 gram.

(4.) 20 c.c. of the solution of sodium nitrite similarly treated yielded—

Volume of nitrogen = 13·79 c.c. Pressure = 256·2 mm. of mercury. Temperature = 16·9° C.
Weight of nitrogen from 10 c.c. of solution = 0·001375 gram.
Weight of nitrous nitrogen in 10 c.c. of solution of sodium nitrite (as determined by standard permanganate) = 0·001346 gram.

The results obtained by both gasometric methods thus not only agree very closely together, but also with the permanganate estimation.

Determination of Nitrous Acid in Presence of Peptones and Ammonia Salts.

On applying the urea-method to the actual solutions in which I wished to determine the nitrous acid, I found that the results obtained were invariably very decidedly low. The solutions in question contained calcium nitrate, invert-sugar, peptone, and carbonate of lime in suspension, besides very minute quantities of calcium chloride, magnesium sulphate, and potassium phosphate. Thus—

Potassium phosphate	0·1	gram	per 1000 c.c.
Magnesium sulphate	0·02	„	
Calcium chloride.....	0·01	„	
Nitrogen (combined in the form of calcium nitrate).....	0·168	„	
Invert-sugar	0·3	„	
Peptone	0·25	„	

This solution was in fact prepared for the cultivation of certain micro-organisms, in order to ascertain their action on the nitric acid

present. Although this solution was in the first instance quite free from ammonia, yet during the growth of some of the micro-organisms under examination ammonia was produced, and it became necessary to have a method for determining the nitrous acid in the presence of the latter.

Experiments were first made by adding known quantities of a standard solution of nitrite to the above solution free from ammonia, which may for convenience be designated as Solution A.

(1.) In the first place, the nitric nitrogen in Solution A was determined by evaporating 10 c.c., and treating the residue by the mercury-method; this gave—

Weight of nitric nitrogen in 10 c.c. Solution A = 0·00337 gram.

(2.) 20 c.c. of a solution of sodium nitrite was similarly treated, the nitrous nitrogen being determined by the mercury-method; this gave—

Weight of nitrogen in 10 c.c. solution of sodium nitrite = 0·001445 gram.

(3.) 20 c.c. of sodium nitrite solution were evaporated, and the nitrous nitrogen determined by the urea-method; this gave—

Weight of nitrogen in 10 c.c. of solution of sodium nitrite = 0·001405 gram.

A mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite solution was evaporated, and the nitrous and nitric nitrogen in the residue determined by the mercury-method; this gave—

Total weight of nitrogen = 0·00277 gram,

if from this the nitric nitrogen in the 5 c.c. of Solution A is subtracted, only 0·001085 gram N is left for the 10 c.c. of sodium nitrite.

(5.) A similar mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite solution was evaporated, and the nitrous nitrogen determined by the urea-method; this gave—

Nitrous nitrogen = 0·00104 gram.

this coincides, therefore, very closely with the amount found by difference in the previous experiment.

(6.) A similar mixture of 5 c.c. Solution A and 10 c.c. of the sodium nitrite, treated similarly to (5), gave—

Nitrous nitrogen = 0·00103 gram.

(7.) Another experiment was made to see whether the amount of

nitrous nitrogen lost was diminished by increasing the proportion of nitrite to Solution A. For this purpose, a mixture of 5 c.c. Solution A and 20 c.c. of sodium nitrite was evaporated, and the nitric and nitrous nitrogen determined together by the mercury-method. The result was—

Total nitrogen = 0·00412 gram.

Subtracting the nitric nitrogen of the 5 c.c. Solution A, the nitrous nitrogen left amounts to 0·002435 gram for the 20 c.c. sodium nitrite employed, or 0·001218 gram for 10 c.c.

Thus, by increasing the proportion of nitrite to a given quantity of Solution A, the proportional loss of nitrous nitrogen is diminished.

From rough experiments, in which the nitrogen evolved by the urea-method was measured in the common nitrometer, I have every reason to believe that the ingredient of Solution A which causes the loss of nitrous nitrogen on evaporation, is the peptone and not the invert-sugar. In fact, possibly the peptone and nitrite enter into a reaction of a similar kind to that which takes place when a solution of an alkaline nitrite is heated with a solution of an ammonium salt, thus—

$$NH_4Cl + NaNO_2 = N_2 + NaCl + 2OH_2.$$

It occurred to me that such an action of the peptone might possibly be counteracted by the presence of an excess of caustic alkali during the evaporation of the solution on the water-bath. To ascertain whether this was the case or not, the following experiments were made:—

(1.) 20 c.c. of standard sodium nitrite were mixed with 10 c.c. of Solution A, and 2 drops of a strong solution of caustic potash (1 : 2) were added to the mixture which was then evaporated to dryness, and the nitrous nitrogen determined by the urea-method. The result was—

Volume of nitrogen = 13·79 c.c. Pressure = 258·2 mm. of mercury. Temperature = 16·4° C.
Nitrous nitrogen per 10 c.c. = 0·001388 gram.

(2.) A perfectly similar mixture to which no potash had been added, gave—

Volume of nitrogen = 13·79 c.c. Pressure = 216·7 mm. of mercury. Temperature = 16·8° C.
Nitrous nitrogen per 10 c.c. = 0·0011631 gram.

(3.) 10 c.c. of the sodium nitrite solution alone, gave—

Volume of nitrogen = 13·79 c.c. Pressure = 127·5 mm. of mercury. Temperature = 17·7° C.
Nitrous nitrogen per 10 c.c. = 0·0013645 gram.

From these experiments, it is evident that the addition of the caustic potash had entirely prevented the loss of nitrous nitrogen during the evaporation of the nitrite with the peptone.

The influence of ammonia salts on the determination of nitrous acid had next to be ascertained. For this purpose, the following experiments were made:—

(1.) 25 c.c. of the standard solution of sodium nitrite (0·001346 gram N per 10 c.c.) were added to 5 c.c. of a standard solution of ammonium chloride (1·5735 grams NH_4Cl per litre), four drops of the strong solution of caustic potash being added to the mixture; this was then evaporated to dryness, and the nitrous nitrogen determined by the urea-method. The result was—

Volume of nitrogen = 13·79 c.c. Pressure = 317·0 mm. of mercury. Temperature = 13·8° C.
Nitrous nitrogen per 10 c.c. = 0·0013754 gram.

(2.) 25 c.c. of sodium nitrite, with 10 c.c. of ammonium chloride and four drops of caustic potash, were treated in a precisely similar manner:—

Volume of nitrogen = 13·79 c.c. Pressure = 311·2 mm. of mercury. Temperature = 14·4° C.
Nitrous nitrogen per 10 c.c. = 0·0013474 gram.

(3.) 25 c.c. of the sodium nitrite solution were evaporated with 10 c.c. of the ammonium chloride without any addition of caustic potash. On treating the residue according to the urea-method, not a trace of gas was evolved, showing that the whole of the nitrous nitrogen had been dissipated by evaporation with ammonium chloride.

From experiments (1) and (2), however, it is evident that the quantity of caustic potash there added had been quite sufficient to prevent any destruction of nitrous nitrogen during evaporation.

Finally, a series of experiments was made in order to ascertain whether in a mixture containing nitrates, nitrites and ammonia, the nitrate could be determined by the mercury-method after evaporating the solution to dryness with an excess of ammonium chloride, and the nitrite by the urea-method after evaporating with an excess of caustic potash. Thus—

(1.) 10 c.c. of a solution of calcium nitrate were evaporated and the nitric nitrogen determined by the mercury-method; this gave—

Volume of nitric oxide = 22·63 c.c. Pressure = 306·6 mm. of mercury. Temperature = 17·2° C.
Weight of nitric nitrogen per 10 c.c. = 0·0053937 gram.

(2.) Ditto in every respect.

Volume of nitric oxide = 22·63 c.c. Pressure = 310·4 mm. of mercury. Temperature = 17·7° C.
Nitric nitrogen per 10 c.c. = 0·005451 gram.

The strength of the solution of calcium nitrate may thus be taken as 10 c.c. = 0·00542 gram nitrogen.

(3.) 20 c.c. of a solution of sodium nitrite were evaporated, and the nitrous nitrogen determined by the urea-method; thus—

Volume of nitrogen = 13·79 c.c. Pressure = 249·7 mm. of mercury. Temperature = 15·5° C.
Nitrous nitrogen per 10 c.c. = 0·001346 gram.

(4.) 10 c.c. of the solution of calcium nitrate with 20 c.c. of the solution of sodium nitrite, and 20 c.c. of solution of ammonium chloride (1·5735 gram NH_4Cl per litre), were evaporated to dryness on the water-bath, and the nitric nitrogen determined by the mercury-method. Thus—

Volume of nitric oxide = 13·79 c.c. Pressure = 512·4 mm. of mercury. Temperature = 15·1° C.
Nitric nitrogen per 10 c.c. = 0·0055335 gram.

(5.) Ditto in every respect.

Volume of nitric oxide = 13·79 c.c. Pressure = 511·2 mm. of mercury. Temperature = 16·9° C.
Nitric nitrogen per 10 c.c. = 0·005485 gram.

(6.) 10 c.c. of the solution of calcium nitrate with 20 c.c. of the solution of sodium nitrite, and 10 c.c. of ammonium chloride were evaporated with five drops of strong caustic potash, the nitrous nitrogen being then determined by the urea-method. Thus—

Volume of nitrogen = 13·79 c.c. Pressure = 268·4 mm. of mercury. Temperature = 14·5° C.
Nitrous nitrogen per 10 c.c. = 0·001452 gram.

(7.) Ditto in every respect.

Volume of nitrogen = 13·79 c.c. Pressure = 259·2 mm. of mercury. Temperature = 15·0° C.
Nitrous nitrogen per 10 c.c. = 0·001400 gram.

These results show that the difficult task of quantitatively determining nitric and nitrous acids in the presence of ammonia can be

satisfactorily accomplished by means of the mercury- and urea-methods respectively, the destruction of the nitrous acid on the one hand being effected by means of an excess of ammonium chloride, whilst on the other hand all loss of nitrous acid can be avoided by evaporation with excess of caustic alkali.

This mode of procedure has a great advantage over all differential methods of determining nitrous and nitric acids, as each acid is determined individually and quite independently of the other.

The urea-method of determining nitrous acid as described above, is both convenient, rapid, and trustworthy, and is suitable for all cases in which only small quantities of nitrous acid are available.

The method may also be adapted for use with the common nitrometer when larger quantities of nitrite are present.

XXVIII.—*The Action of some Specific Micro-organisms on Nitric Acid.*

By Percy F. Frankland, Ph.D., B.Sc., F.S.C., Associate Royal School of Mines.

That nitric acid may be reduced to nitrous acid by the agency of bacteria appears to have been first shown in 1875 by Meusel (*Ber.*, **8**, 1215), who found that well-water containing nitrates and bacteria, on standing for some days, gave a definite reaction for nitrous acid, which was prevented by the addition of antiseptic substances, such as salicylic, carbolic, or benzoic acids. He also found that on adding nitrates and carbohydrates to water containing bacteria, the nitrates soon became converted into nitrites.

In 1882, Gayon and Dupetit (*Ber.*, **15**, 1882, 2736) describe the reduction of nitrates by "anaërobic" micro-organisms. Again in the same year, Déhérain and Maquenne (*Ber.*, **15**, 1882, 3081) ascribe the reduction of nitrates in the soil to the agency of the butyric ferment, the so-called *Bacillus amylobacter*.

In 1883, Gayon and Dupetit (*Ber.*, **16**, 1883, 221; *Compt. rend.*, **95**, 1365) further describe the decomposition of nitrates by other anaërobic micro-organisms.

The reduction of nitrates by micro-organisms is also frequently referred to by Warington in his well-known researches on nitrification, and has been also confirmed and elaborated by Munro (Trans., 1886, 632).

Heraeus (*Zeitschr. f. Hygiene*, 1886, 193), has also made experi-

ments on the reduction of nitrates by micro-organisms, and these appear to be the first in which pure cultivations, obtained by the modern methods of separation and isolation, which can alone guarantee the absolute purity of the cultures, have been employed. To these experiments, further reference will be made later on.

With few exceptions, however, all the experiments referred to above have been made, not with pure cultivations of well-characterised micro-organisms, but with casual mixtures of microbes such as are obtained from soil, sewage, natural waters, and the like.

In the course of investigations, which I have now been carrying on for some years past, on the micro-organisms present in the atmosphere and in natural waters, I have had occasion to collect a number of micro-organisms from these sources, to cultivate them in a state of purity, and to characterise them in such detail that they may be readily identified by subsequent observers. It appeared to me, therefore, very desirable that the action of these aërial and aquatic micro-organisms on nitrates should be carefully studied, more especially as there has been some tendency to believe that nearly all microbes possess the property of decomposing nitrates if placed under suitable conditions.

Method of Experiment.

The nitric acid, submitted to the action of the various micro-organisms, was in combination as calcium nitrate contained in a solution capable of nourishing the microbes. In the first instance, solutions were employed in which the only nitrogen present was the nitric nitrogen of the calcium nitrate, but in such solutions the growth of the micro-organisms was so uncertain that it was found necessary to introduce a small proportion of peptone, although thereby somewhat complicating the composition of the nutritive liquid.

The solution which ultimately appeared most suitable for the purpose had the following composition:—

Potassium phosphate	0·1	gram	in 1000 c.c. of distilled water with 4 grams of pure calcium carbonate in suspension.
Magnesium sulphate (cryst.)..	0·02	,,	
Calcium chloride (fused)	0·01	,,	
Nitrogen (combined in the form of calcium nitrate)	0·168	,,	
Invert sugar.....	0·3	,,	
Peptone	0·25	,,	

This solution was poured into sterilised bottles, plugged with sterile cotton-wool, so that each bottle was from three-fourths to five-sixths filled with liquid. The bottles so filled were then finally sterilised by steaming for one hour on four successive days.

The solution thus prepared gave no reaction either with Nessler's solution or with the sulphanilic acid and phenol test for nitrous acid.

Into these sterilised solutions, the particular micro-organisms were inoculated with a platinum needle, the cotton-wool stopper being singed in a Bunsen flame just before extracting it to permit of the introduction of the platinum needle, the stopper being then immediately replaced when the inoculation was complete.

Of the micro-organisms experimented with, those derived from air have been fully described by me (*Roy. Soc. Phil. Trans.*, 1887, **178**, B, 257—287), whilst those derived from water will shortly be similarly described.

First Series of Experiments.

A series of bottles containing the above solution were inoculated in the way described with the various micro-organisms mentioned below; the inoculated bottles were then placed in the incubator and kept at a temperature of 30° C., and submitted to examination after the specified intervals of time. In examining the solutions, a number of pipettes which had been steam-sterilised were kept in readiness, the cotton-wool plug of the bottle to be opened was singed in a Bunsen, then withdrawn with a pair of forceps, and the sterile pipette introduced, and by means of it a few cubic centimetres of the liquid taken out, the cotton-wool plug being then immediately replaced.

The results of this first examination (table, p. 376) showed at once that there exist very marked differences in the behaviour of different micro-organisms towards nitrates. Thus, whilst some of the organisms in question had in the course of three days converted a large amount of nitrate into nitrite, others had given rise to the production of no nitrite at all, whilst the growth of others again had resulted in the formation of only traces of nitrous acid. It is moreover noticeable that these differences are by no means dependent upon the greater or less vigour of the growth to which the several organisms give rise in this medium. Thus many of the organisms, such as *B. viscosus*, *nubilus*, *subtilis*, produce strong visible growths in the solution, rendering the latter excessively turbid or producing flocculent deposits, without giving rise to the formation of any nitrite.

It is, moreover, very noticeable that all the organisms, without exception, which give rise to the production of an appreciable amount of nitrous acid are bacilli, whilst not one of the micrococci examined gives rise to more than a doubtful indication of nitrite.

Again, it is very remarkable how differently two organisms like *B. subtilis* and *B. cereus*, which in their microscopical and other morphological characters are only with difficulty distinguishable, behave

Examination of Solutions after 3—4 Days' Growth at 30°.

Name of micro-organism.	Origin.	Appearance of solution.	Reaction with sulphanilic acid, phenol, and ammonia.
Bacillus ramosus ..	Water	Liquid clear, but abundant membranous growths on sides of bottle	Very strong.
B. violaceus	,,	Liquid very slightly turbid, numerous violet lumps on bottom of bottle	Very strong.
B. vermicularis	,,	Liquid very turbid, but not much deposit	Strong.
B. nubilus	,,	Liquid turbid, not much deposit	None.
B. viscosus	,,	Liquid turbid, not much deposit	None.
B. aquatilis	,,	Liquid very turbid, not much deposit	Very faint.
B. liquidus	,,	Liquid turbid, not much deposit	Strong.
B. arborescens	,,	No visible growth	None.
B. aurantiacus	,,	No visible growth	None.
B. cereus.....	Air	Liquid not very turbid, but considerable flocculent deposit	Strong.
B. subtilis.....	,,	Ditto	None.
B. lævis	,,	Liquid turbid, not much deposit	None.
B. pestifer	,,	Liquid very turbid, not much deposit	Very strong.
B. plicatus.....	,,	Liquid very slightly turbid, little or no deposit	Very strong.
B. prodigiosus.....	,,	Liquid turbid, not much deposit	Strong.
B. aurescens	,,	Liquid not very turbid, but some yellow deposit	Decided.
B. aureus	,,	Liquid very turbid, and considerable yellow deposit	Faint.
B. fluorescens	,,	Liquid very turbid, not much deposit	Distinct.
B. chlorinus	,,	Ditto	Distinct.
B. citreus	,,	Liquid very slightly turbid, a little yellow deposit	Distinct.
B. profusus.....	,,	Liquid slightly turbid, not much deposit	None.
B. polymorphus....	,,	Liquid scarcely turbid	None.
Sarcina aurantiaca.	,,	Liquid very turbid, not much deposit	None.
Sarcina lutea.....	,,	Ditto	None.
Sarcina liquefaciens	,,	Liquid slightly turbid, distinct deposit	None.
Streptococcus liquefaciens	,,	Liquid very slightly turbid	None.
Micrococcus rosaceus	,,	Liquid turbid, not much deposit	Very faint.
M. carnicolor	,,	Ditto	None.
M. gigas.....	,,	Ditto	None.
M. albus	,,	Liquid very slightly turbid	None.
M. candicans.....	,,	Ditto	None.
M. chryseus	,,	Liquid almost perfectly clear	None.
Blank experiment ..	—	Liquid perfectly clear	None.

Examination of the same Solutions after 41 *Days' Growth.*

Name of micro-organism.	Origin.	Appearance of solution.	Reaction with diphenylamine.	Reaction with sulphanilic acid, phenol, and ammonia.
*B. ramosus**	Water	Liquid quite clear, much flocculent deposit	Strong	Strong yellow-red.
*B. violaceus**	,,	Liquid nearly clear. Considerable violet deposit	,,	Strong yellow-red.
*B. vermicularis** .	,,	Liquid slightly opalescent. Not much deposit	,,	Strong yellow-red.
*B. nubilus**	,,	Liquid almost clear	,,	Straw colour.
B. viscosus	,,	Ditto	,,	None.
*B. aquatilis**	,,	Liquid slightly opalescent	,,	Very faint indeed.
*B. liquidus**	,,	Liquid slightly turbid	,,	Strong yellow-red.
B. arborescens— .	,,	Liquid quite clear	,,	None.
*B. aurantiacus** .	,,	Liquid almost clear. Orange deposit	,,	None.
*B. cereus**	Air	Liquid nearly clear. Much flocculent deposit	,,	Strong yellow-red.
*B. subtilis**	,,	Ditto	,,	None.
*B. lævis**	,,	Liquid nearly clear	,,	None.
*B. pestifer**	,,	Ditto	,,	Strong yellow-red.
B. plicatus—	,,	Ditto	,,	,,
B. prodigiosus + .	,,	Liquid slightly opalescent	,,	,,
B. aurescens— ..	,,	Liquid very turbid. Some yellow deposit	,,	Faint straw.
B. aureus—	,,	Liquid very turbid. Considerable orange deposit	,,	,,
B. fluorescens— .	,,	Liquid almost clear	,,	Strong yellow.
*B. chlorinus**	,,	Liquid opalescent. Some yellow deposit	,,	Straw.
B. citreus—	,,	Liquid clear	,,	Strong yellow.
B. profusus— ...	,,	Liquid almost clear	,,	Straw.
B. polymorphus—	,,	Liquid quite clear	,,	None.
Sarcina aurantiaca—	,,	Liquid very turbid. Some yellow deposit	,,	None.
*Sarcina lutea** ..	,,	Ditto	,,	None.
*Sarcina liquefaciens**	,,	Liquid very turbid	,,	None.
*Streptococcus liquefaciens**	,,	Liquid clear	,,	None.
M. rosaceus— ...	,,	Liquid very opalescent. Little red deposit	,,	Pale straw.
M. carnicolor— .	,,	Liquid slightly opalescent. No red colour	,,	Strong yellow.
M. gigas	,,	Liquid almost clear	,,	None.
M. albus—	,,	Liquid clear	,,	None.
M. candicans— ..	,,	Liquid almost clear	,,	None.
M. chryseus + ...	,,	Ditto	,,	None.
Blank exprnt.—..	—	Liquid perfectly clear	,,	None.

towards nitrates; thus, whilst *B. cereus* reduces the nitrate powerfully, *B. subtilis* yields no nitrite whatever, and thus the two organisms become most sharply distinguishable on being submitted to this chemical test.

The solutions tested as above were now allowed to remain at the ordinary temperature of the laboratory (about 20°) until they were again examined 41 days after their first inoculation (table, p. 377).

Thus the longer preservation of the solutions had produced no marked difference in the results. The solutions which gave a strong reaction for nitrous acid after three days' growth still gave the same, and those which gave no reaction in the former examination were still free from nitrite after 41 days, excepting in the case of *M. carnicolor*, which, though free from nitrite before now, gave a distinct reaction. Further experiments have shown that this organism, *M. carnicolor*, does slightly reduce the nitrate, and, moreover, in a more marked manner than the very similar *M. rosaceus*, which in no case gave more than a very faint indication of nitrite.

The fact that all the solutions gave strong reactions with diphenylamine shows that in no case had the oxidised nitrogen been destroyed, that is, completely reduced to ammonia, assimilated as organic nitrogen, or eliminated as free nitrogen or oxide of nitrogen.

The solutions were again examined after another interval, the total length of time since inoculation being now 137 days; the reactions for nitrous acid were practically identical with those given in the last series, and need not, therefore, be repeated. The solutions were, however, on this occasion also tested for ammonia with Nessler's solution, with which they were found to exhibit great differences. Thus, in the above solutions those which yielded a strong reaction with the Nessler test are marked*, whilst those which yielded a distinct but not very strong one are marked +, and those which yielded practically no reaction are marked —.

Second Series of Experiments.

In order to determine whether the results obtained in the former series of experiments were constant for the particular micro-organisms or merely accidental, a number of similar solutions were inoculated with some of the micro-organisms which had produced the most striking results. After three days' growth in the incubator at 30°, these inoculated solutions were submitted to examination with Nessler's test, with the diphenylamine test, and by means of sulphanilic acid, phenol, and ammonia. Thus:—

Examination of Solutions after three Days' Growth at 30°.

Name of micro-organism.	Appearance of solution.	Reactions with		
		Diphenyl-amine.	Sulphanilic acid.	Nessler.
B. ramosus....	Liquid quite clear, but numerous tufts over sides and bottom of bottle	Very deep blue	Very strong yellow-red	Strong.
B. cereus.....	Abundant flocculent matter and deposit	Ditto	Ditto	Fairly strong.
B. subtilis	Abundant flocculent deposit	Ditto	None	Ditto.
B. viscosus	Liquid very opalescent, little or no deposit	Ditto	None	None.
B. chlorinus ..	Ditto	Ditto	Strong chrome-yellow	Very strong.
M. rosaceus ...	Ditto	Ditto	Faint	Slight.
M. carnicolor..	Liquid very opalescent, very slight flocculent deposit	Ditto	Chrome-yellow colour	Slight.
Blank experiment	Liquid quite clear	Ditto	None	None.

Thus in each case the previous results were confirmed.

Quantitative Experiments.

Having thus by the above experiments determined which micro-organisms give rise to the reduction of nitrates to nitrites, a number of quantitative experiments were now made in order to ascertain the manner in which the nitrogen was distributed in the forms of nitrate, nitrite, and ammonia after the growth of the several organisms.

The determinations of nitrate and nitrite were made on the lines laid down in my previous communication "On the Determination of Nitrous Acid," the nitric acid being estimated by the measurement of the nitric oxide gas obtained by decomposition with mercury, whilst the nitrous acid was estimated by measuring the nitrogen liberated by the action of urea and dilute sulphuric acid.

For the purpose of these determinations, 10 c.c. of the solutions were in each case taken, and on this account the actual results obtained for this volume of solution are given below, as well as those calculated to parts per 100,000.

The accurate determination of ammonia in solutions of this kind is attended with great difficulty owing to the presence of basic products

other than ammonia; these give colorations with the Nessler-test which cannot be satisfactorily compared with those obtained with a standard solution of ammonium chloride, owing to the difference in the colours. The estimations of ammonia cannot, therefore, lay claim to any great degree of accuracy, but they serve to indicate certain broad differences in the action of the various micro-organisms. These determinations of ammonia were made by diluting a measured volume of the solution (the exact volume taken depending upon the proportion of ammonia present) with distilled water free from ammonia, and then nesslerising.

The first series of quantitative experiments was made with a number of solutions which remained in the incubator at 30° for 26 days, and then for nine days more at the ordinary temperature of the laboratory (about 16—18°) before they were submitted to examination. With these solutions, the following results were obtained.

Blank Experiment.—The liquid was clear and transparent.

(*a.*)	10 c.c. yielded	0·003342	gram	nitrogen as nitrate.
(*b.*)	10 „	0·003384	„	„
(*c.*)	10 „	0·003324	„	„
(*d.*)	10 „	0·003451	„	„
	Mean	0·003375	„	„

or 33·75 *parts of nitric nitrogen per* 100,000 *parts of solution.*

Note.—This solution was prepared with twice the quantity of calcium nitrate mentioned on p. 374.

The solution was free from ammonia and nitrites.

Bacillus vermicularis.—The liquid was very opalescent with a fine deposit at the bottom, it yielded strong reactions for ammonia and nitrous acid.

10 c.c. yielded	0·0012907	gram	nitric nitrogen.
„	0·0021143	„	nitrous nitrogen.
„	0·0034050	„	nitrogen as nitrates and nitrites.

Ammoniacal nitrogen in 10 c.c. = 0·000326 gram.

Parts per 100,000	Nitric nitrogen	12·91
	Nitrous nitrogen	21·14
	Ammoniacal nitrogen ..	3·26

Bacillus pestifer.—The liquid gave very strong reactions for ammonia and nitrous acid.

10 c.c. yielded	0·001069	gram	nitric nitrogen.
„	0·002285	„	nitrous nitrogen.
„	0·003354	„	nitrogen as nitrates and nitrites.

Ammoniacal nitrogen in 10 c.c. = 0·000412 gram.

Parts per 100,000	Nitric nitrogen	10·69
	Nitrous nitrogen	22·85
	Ammoniacal nitrogen ..	4·12

Bacillus ramosus.—The liquid was clear but contained abundance of characteristic tufted growths; it gave strong reactions for ammonia and nitrous acid.

10 c.c. yielded 0·001668 gram nitric nitrogen.
„ 0·001646 „ nitrous nitrogen.
„ 0·003314 „ nitrogen as nitrates and nitrites.

Ammoniacal nitrogen in 10 c.c. = 0·000309 gram.

Parts per 100,000	Nitric nitrogen	16·68
	Nitrous nitrogen	16·46
	Ammoniacal nitrogen ..	3·09

Bacillus prodigiosus.—The liquid was very opalescent, but there was not much deposit; it gave strong reactions for ammonia and nitrous acid.

10 c.c. yielded 0·0020355 gram nitric nitrogen.
„ 0·0011931 „ nitrous nitrogen.
„ 0·0032286 „ nitrogen as nitrates and nitrites.

Ammoniacal nitrogen in 10 c.c. = 0·000515 gram.

Parts per 100,000	Nitric nitrogen	20·36
	Nitrous nitrogen	11·93
	Ammoniacal nitrogen ..	5·15

Bacillus liquidus.—The liquid gave very strong reactions for ammonia and nitrous acid.

10 c.c. yielded 0·002042 gram nitric nitrogen.
„ 0·001134 „ nitrous nitrogen.
„ 0·003176 „ nitrogen as nitrates and nitrites.

Ammoniacal nitrogen in 10 c.c. = 0·00068 gram.

Parts per 100,000	Nitric nitrogen	20·42
	Nitrous nitrogen	11·34
	Ammoniacal nitrogen ..	6·80

Bacillus plicatus.—The liquid gave no ammonia reaction, but a strong one for nitrous acid.

10 c.c. yielded 0·002550 gram nitric nitrogen.
„ 0·000504 „ nitrous nitrogen.

„ 0·003054 „ nitrogen as nitrates and nitrites.

Parts per 100,000	Nitric nitrogen	25·50
	Nitrous nitrogen	5·04
	Ammoniacal nitrogen ..	0

Bacillus fluorescens.—The liquid gave practically no reaction for ammonia, and not a strong one for nitrous acid.

10 c.c. yielded 0·0032322 gram nitric nitrogen.
„ 0·0000797 „ nitrous nitrogen.

„ 0·0033119 „ nitrogen as nitrates and nitrites.

Parts per 100,000	Nitric nitrogen	32·32
	Nitrous nitrogen	0·80
	Ammoniacal nitrogen ..	0

Sarcina lutea.—The liquid was very opalescent with a fine yellowish deposit. It gave a very strong reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·0029928 gram nitric nitrogen.
Ammoniacal nitrogen in 10 c.c. = 0·000371 gram.

Parts per 100,000	Nitric nitrogen	29·93
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	3·71

Bacillus aquatilis.—The liquid was very opalescent, with little or no deposit. It gave a strong reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·002597 gram nitric nitrogen.
Ammoniacal nitrogen in 10 c.c. = 0·000261 gram.

Parts per 100,000	Nitric nitrogen	25·97
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	2·61

The above results may be conveniently summarised in the following table, which also records the results of some determinations of ammonia made in solutions in which little or no nitrous acid had been produced by the action of the micro-organisms:—

Quantitative Results of Growth of Micro-organisms during 35 Days.

Name of micro-organism.	Parts per 100,000.			
	Nitric nitrogen.	Nitrous nitrogen.	Nitrogen as nitrates and nitrites.	Ammoniacal nitrogen.
Blank experiment ...	33·75	0	33·75	0
B. vermicularis	12·91	21·14	34·05	3·26
B. pestifer	10·69	22·85	33·54	4·12
B. ramosus	16·68	16·46	33·14	3·09
B. prodigiosus	20·36	11·93	32·29	5·15
B. liquidus	20·42	11·34	31·76	6·80
B. plicatus	25·50	5·04	30·54	0
B fluorescens	32·32	0·80	33·12	0
Sarcina lutea	29·93	0	29·93	3·71
B. aquatilis	25·97	0	25·97	2·61
Sarcina aurantiaca..	Not determined	0	—	0·34
B. aurantiacus	„	trace	—	2·06
B. aurescens	„	„	—	0·26
B. aureus	„	„	—	0·82
B. viscosus	32·63	0	32·63	0·52

From the above table, it will be seen that in no case was the nitric acid of the original solution completely reduced, and in those cases in which notable proportions of nitrous acid were produced, the sum of the nitrous and nitric nitrogen was almost exactly equal to the nitric nitrogen in the original solution, the ammonia in these cases being apparently derived from the decomposition of the peptone contained in the original solution. The peptone in the original solution amounted to 25 parts per 100,000, and it was found by combustion with soda-lime that the peptone employed contained 13·65 per cent. of nitrogen; there would, therefore, be 3·41 parts of peptone-nitrogen per 100,000, which, considering the impossibility of making accurate determinations of ammonia in liquids of this kind, does not differ very materially from even the largest proportions of ammoniacal nitrogen found in the solutions. There is, in fact, no evidence of the nitrate in the original solution being largely reduced to ammonia in any case.

The following three experiments are of interest, as showing how the reduction of the nitrate to nitrite may become complete, and confirming the above opinion that none of the oxidised nitrogen is reduced to ammonia. These experiments were made with a solution having the same composition as the one used in the above experiments, only with less calcium nitrate in it. The solutions were

inoculated with *Bacillus subtilis*, *B. cereus*, and *B. ramosus*, the nitric acid being also determined in a portion of the solution not inoculated.

Blank Experiment.—This gave 19·30 parts nitric nitrogen per 100,000.

B. subtilis.—The solution was examined 70 days after inoculation. The *nitric* nitrogen only was determined, as it gave no reaction for nitrous acid.

10 c.c. gave 0·001950 gram nitric nitrogen, or 19·50 parts of nitric nitrogen per 100,000.

B. cereus.—This also was examined 70 days after inoculation. The *nitrous* nitrogen only was determined.

10 c.c. gave 0·001962 gram nitrous nitrogen, or 19·62 parts nitrous nitrogen per 100,000.

B. ramosus.—This also was examined 70 days after inoculation. The *nitrous* nitrogen only was determined.

10 c.c. gave 0·001968 gram nitrous nitrogen, or 19·68 parts nitrous nitrogen per 100,000.

Thus the solution in which the *B. subtilis* had flourished retained its nitrate quite unchanged, although from numerous other experiments we know that a notable proportion of ammonia must have been formed, and this must consequently have been derived from the organic nitrogen of the peptone.

The whole of the original nitric nitrogen, on the other hand, was found as nitrous nitrogen in the solutions in which *B. cereus* and *B. ramosus* had flourished, so that the ammonia which numerous other experiments show to have been produced in these solutions, must have been derived from the organic nitrogen of the peptone.

Experiments with Exclusion of Air.

In all the experiments hitherto described, the bottles containing the solutions were plugged with cotton-wool only, so that more or less free circulation of air was possible. Experiments were now made in order to ascertain whether, if access of air to the solutions was prevented, materially different results would follow. For this purpose, immediately after inoculation, the cotton-wool plugs were cut down so as to be flush with the neck of the bottle; a quantity of melted wax was then allowed to drop on to the cut surface of the plug until the bottle was completely sealed, and the surface of the wax was then further thickly coated with cerate.

For these experiments, a number of those micro-organisms were

taken which had in the previous experiments exerted no reducing action on the nitrate, and which it was thought might possibly do so when air was wholly excluded in this manner.

The inoculated bottles were kept in the incubator at 30° for 14 days, and they then remained 21 days longer at the ordinary temperature of the laboratory (16—18°) before examination. The solutions were thus 35 days old when the following results were obtained :—

Bacillus subtilis.—The liquid was quite clear, but abundance of flocculent matter had collected on the bottom of the bottle. The liquid gave a strong reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·003349 gram nitric nitrogen.
„ „ 0·000168 „ ammoniacal nitrogen.

Parts per 100,000	Nitric nitrogen	33·49
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	1·68

Thus, just as in the previous experiments with this micro-organism, the nitric nitrogen remained wholly unaffected by its growth.

Bacillus lævis.—The liquid was slightly opalescent; some flaky matter had collected at the bottom of the bottle. The liquid gave a distinct reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·003379 gram nitric nitrogen.
„ „ 0·000027 „ ammoniacal nitrogen.

Parts per 100,000	Nitric nitrogen	33·79
	Nitrous nitrogen.....	0
	Ammoniacal nitrogen ..	0·27

Thus, as before, the nitric nitrogen had remained wholly unaffected by the growth of this organism.

Sarcina liquefaciens.—The liquid had become quite clear, but some fine deposit had collected on the bottom of the bottle. The liquid gave a distinct reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·003360 gram nitric nitrogen.
„ „ 0·000049 „ ammoniacal nitrogen.

Parts per 100,000	Nitric nitrogen	33·60
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	0·49

In this case again, the exclusion of air had not altered the result, the nitric nitrogen remaining quite unaffected by the growth of the organism.

Sarcina aurantiaca.—The liquid was slightly opalescent, with a considerable yellow, flocculent deposit. It gave a strong reaction for ammonia, but none for nitrous acid.

10 c.c. yielded 0·003420 gram nitric nitrogen.
„ „ 0·000057 „ ammoniacal nitrogen.

Parts per 100,000	Nitric nitrogen	34·20
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	0·57

The nitric nitrogen had thus again remained quite unaffected.

Micrococcus candicans.—The liquid had become clear, but some deposit had collected at the bottom. There was no reaction either for ammonia or nitrous acid.

10 c.c. yielded 0·003330 gram nitric nitrogen.

Parts per 100,000	Nitric nitrogen	33·30
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	0

In this case again, the vigorous growth of the micro-organism had been without any effect on the nitrate.

Bacillus aquatilis.—The liquid was slightly opalescent with a small amount of deposit; it gave a strong reaction for ammonia, but none for nitrous acid.

(*a.*) 10 c.c. yielded 0·002621 gram nitric nitrogen.
(*b.*) „ „ 0·002597 „ „

Parts per 100,000	Nitric nitrogen	26·09
	Nitrous nitrogen	0
	Ammoniacal nitrogen ..	1·34

The results obtained in this case coincide very closely indeed with those previously obtained when the air was not excluded, and they show that this organism causes the disappearance of a considerable proportion of the nitric nitrogen without any corresponding formation of nitrous acid or ammonia.

Similar experiments were also made with two organisms which had previously been found to effect a powerful reduction of nitric to nitrous acid. Thus:—

Bacillus cereus.—The liquid had become quite clear, but a considerable amount of flocculent matter had collected on the bottom. The liquid gave very strong reactions for ammonia and nitrous acid.

10 c.c. yielded 0·0016467 gram nitric nitrogen.
(*a*.) „ „ 0·0013368 „ nitrous nitrogen.
(*b*.) „ „ 0·0013655 „ „ „
„ „ 0·0002255 „ ammoniacal nitrogen.

Parts per 100,000 { Nitric nitrogen ..... 16·47 / Nitrous nitrogen .... 13·51 } = 29·98.
Ammoniacal nitrogen. 2·26

Bacillus ramosus.—The liquid had become quite clear, but there were the characteristic streaming flocculi on the sides and bottom of the bottle. The solution gave very strong reactions for ammonia and nitrous acid.

10 c.c. yielded 0·001724 gram nitric nitrogen.
(*a*.) „ „ 0·001571 „ nitrous nitrogen.
(*b*.) „ „ 0·001561 „ „ „
„ „ 0·000309 „ ammoniacal nitrogen.

Parts per 100,000 { Nitric nitrogen ..... 17·24 / Nitrous nitrogen .... 15·66 } = 32·90.
Ammoniacal nitrogen. 3·09

Thus in the case of both of these organisms the results are essentially similar whether the air is excluded or not, the nitrate being powerfully reduced to nitrite, whilst an appreciable quantity of ammonia is generated, which, at any rate in the case of *B. ramosus*, appears to be exclusively derived from the organic nitrogen of the peptone.

Experiments with varying Proportions of Peptone and Sugar.

Of those organisms which powerfully reduce nitrates to nitrites, two representatives were taken—*B. ramosus* and *B. pestifer*—and with these further experiments were made with a view to ascertain whether the amount of nitrite formed in a given time was due to the proportion of either peptone or sugar, or of both, present in the solution.

For this purpose, five different solutions were employed, as follows:—

Solution No. 1.—This was the same solution as that employed in the previous experiments, and containing—

Cane-sugar (inverted) ..... 0·30 gram
Peptone ..... 0·25 „ } in 1000 c.c.

Solution Nos. 2, 3, 4, *and* 5.—These differed from No. 1 only in the proportions of sugar and peptone which they contained, thus:—

	2.	3.	4.	5.	
Cane-sugar (inverted)..	0·6 gram	2·4	0·6	2·4	} in 1000 c.c.
Peptone.....	0·25 „	0·25	1·0	1·0	

These five solutions were inoculated with *B. ramosus* and *B. pestifer* respectively, and kept for 19 days in the incubator at 32—33° before examination.

The results obtained may be most conveniently summarised in the following table:—

Parts per 100,000.

Solution I. (Peptone, 0·25 gram; sugar, 0·3 gram.)

	B. ramosus.	*B. pestifer.*
Nitric nitrogen.....	16·74	13·17
Nitrous nitrogen	16·08	22·27
Ammoniacal nitrogen	2·56	2·87

Solution II. (Peptone, 0·25 gram; sugar, 0·6 gram.)

Nitric nitrogen.....	7·13	6·04
Nitrous nitrogen	27·02	28·72
Ammoniacal nitrogen	2·26	1·64

Solution III. (Peptone, 0·25 gram; sugar, 2·4 gram.)

Nitric nitrogen.....	11·71	4·15
Nitrous nitrogen	21·18	29·09
Ammoniacal nitrogen	0·62	0·62

Solution IV. (Peptone, 1·0 gram; sugar, 0·6 gram.)

Nitric nitrogen.....	lost	trace
Nitrous nitrogen	32·11	34·74
Ammoniacal nitrogen	6·15	3·69

Solution V. (Peptone, 1·0 gram; sugar, 2·4 gram.)

Nitric nitrogen.....	0	0
Nitrous nitrogen	32·60	33·98
Ammoniacal nitrogen	3·08	0·41

From this table it is apparent that as the proportion of organic matter, in the shape of sugar and peptone, is increased in these solutions, so the amount of nitrate reduced to nitrite in a given time is also increased. Moreover, the amount of nitrate reduced is far more dependent on the proportion of peptone than on that of sugar.

Thus solutions II and III contain the same proportion of peptone, whilst the sugar in III is four times as great as that in II, yet, notwithstanding, the reduction to nitrite is much the same in both cases, and with *B. ramosus* in fact the reduction is somewhat greater in solution II than in III. Again, solution IV contains four times as much peptone as solution II, whilst the proportion of sugar is the same in both; but whereas a considerable proportion of nitrate is left in solution II, it is practically completely reduced to nitrite in No. IV; or, in other words, whilst the quadrupling of the peptone brings about complete reduction of the nitrate to nitrite (compare solutions II and IV), quadrupling the amount of sugar results in little or no increased reduction of nitrate.

Another point brought out by these experiments is that the ammonia developed in these solutions is due to decomposition of the peptone, and not to reduction of nitric or nitrous acids. Thus solutions I, II, and III all contain the same *small* proportion of peptone, and all yield comparatively small proportions of ammonia; it is, moreover, particularly noticeable that solution III, which contains four times as much sugar as II, yields the smallest proportion of ammonia, whilst solution I, which contains the same amount of peptone but the least sugar, yields the largest proportion of ammonia of the first three solutions; whilst solution IV, which contains four times as much peptone as II, with the same amount of sugar, yields the largest proportion of ammonia of all, and solution V, which contains the same amount of peptone as IV but four times the amount of sugar, yields only a small proportion of ammonia. It appears, therefore, that the maximum yield of ammonia is obtained when the proportion of peptone to sugar is high, and the least when the proportion of peptone to sugar is low.

Action of the various Micro-organisms on Ammoniacal Nitrogen.

In order to ascertain whether any of these organisms possessed the power of oxidising ammoniacal nitrogen to nitrates and nitrites, they were severally inoculated into a solution of the following composition:—

Potassium phosphate.....	0·1	gram	in 1000 c.c. of distilled water with 4 grams of pure calcium carbonate in suspension.
Magnesium sulphate (cryst.).	0·02	„	
Calcium chloride (fused)	0·01	„	
Ammonium chloride	0·5	„	
Cane-sugar (inverted)	0·3	„	
Peptone	0·25	„	

The solutions were examined after 40 days' growth, but in no case was anything more than a faint indication of nitrous acid obtainable with sulphanilic acid, phenol, and ammonia.

It is worthy of notice that Heræus (*Zeitsch. f. Hygiene*, 1886, 229) has experimented with three of the micro-organisms which I have had under observation, viz., *B. subtilis*, *B. prodigiosus*, and *B. ramosus*. On growing these in sterilised urine, he found that *B. subtilis* alone gave no nitrous acid reaction, whilst the other two gave distinct reactions for nitrites; from this he concludes that *B. prodigiosus* and *B. ramosus* possess oxidising powers, and that *B. subtilis* does not. My experiments, however, conclusively prove that both *B. ramosus* and *B. prodigiosus* exert a reducing action, whilst *B. subtilis* does not; and therefore that the nitrous acid reactions which he obtained in the case of the two former organisms, must obviously have been due to the reduction of the nitrate in the urine, and not to oxidation of ammoniacal nitrogen as he supposes. That nitric nitrogen is an invariable constituent of human urine has been shown by Warington (Trans., 1884, 669), and has in fact been long known.

The principal results arrived at in this investigation may be summarised as follows:—

1. That there is a great difference in the power possessed by micro-organisms of reducing nitric acid. Of the 32 forms under examination, 16 or 17 were found to reduce nitric to nitrous acid more or less completely, whilst 15 or 16 were quite destitute of this power.

2. That this difference in reducing power may in certain cases be of great value in distinguishing between micro-organisms morphologically very similar.

3. The behaviour of the various micro-organisms in question was not altered in this respect by preventing access of air to the solutions in which they were cultivated.

4. In no case did the reducing action lead to the formation of any considerable amount of ammonia, the development of ammonia in the solutions being due principally, if not wholly, to the decomposition of the peptone.

5. In the case of two of the organisms possessing a strong reducing power, it was found by more detailed experiments that the quantity of nitrate reduced to nitrite in a given time was dependent on the proportion of organic matter—peptone and sugar—present in the solution, the peptone exerting a far greater influence in this respect than the sugar.

6. In these special experiments mentioned above, it was found that the development of ammonia was dependent upon the peptone and sugar present, the amount of ammonia formed being greatest with

the highest proportion of peptone to sugar, and least with the greatest proportion of sugar to peptone.

7. In nearly all cases in which partial or total reduction of nitrate to nitrite had taken place, the sum of the nitrogen as nitrate and nitrite in the "fermented" solution was practically identical with the nitric nitrogen in the original "unfermented" solution, whilst in those cases in which no reduction to nitrite took place, the nitrate in the solution remained practically unaffected by the growth of the micro-organism. In one case, however, it was found that an organism, *B. aquatilis*, which does not reduce nitrates to nitrites, caused by its growth the disappearance of a considerable proportion of nitric nitrogen, this result being confirmed by a second experiment.

8. None of the organisms under examination were found capable of oxidising ammoniacal nitrogen to nitrous or nitric acids when introduced into a nutritive solution containing ammonium chloride.

XXIX.—*Action of Alcohols on Ethereal Salts in Presence of Small Quantities of Sodic Alkylate.*

By T. Purdie, Ph.D., B.Sc., Professor of Chemistry in the University of St. Andrews, and W. Marshall, B.Sc.

Considering the close analogy existing between metallic and ethereal salts on the one hand, and metallic hydroxides and alcohols on the other, it might well be expected that the chemical change, ordinarily called double decomposition, so constantly exhibited by metallic salts and bases, would also be of frequent occurrence among their organic analogues, the ethereal salts and alcohols.

Various isolated instances of interchange of alcoholic radicle occurring between ethereal salts and alcohols have been recorded. The probability of a double decomposition of this kind taking place in the course of operations on ethereal salts in alcoholic solution is indeed commonly recognised, and provided for by employing the alcohol containing the same radicle as the ethereal salt operated on; but, so far as we are aware, these reactions have not, except in a few instances, been made the subject of special study.

Friedel and Crafts (*Annalen*, **130**, 198; **133**, 207) heated various mixtures of alcohols and ethers, amongst others, mixtures of ethylic acetate with amylic alcohol, and amylic acetate with ethylic alcohol,

and found that in each case interchange of radicle occurred. They concluded that this interchange was not due to varying specific affinities of the alcohols, but was to be attributed rather to the influence of mass.

Röse (*Annalen*, **205**, 240) has shown, on the other hand, that in the case of the ethereal carbonates the alcohol of higher molecular weight can displace almost entirely the alcohol of lower molecular weight, while the converse reaction takes place to only a small extent.

A. Bachmann (*Annalen*, **218**, 50) heated methylic and ethylic acetates with various alcohols of the $C_nH_{2n+1}OH$ series to the boiling point of the higher boiling substance, and did not observe any action.

G. Bertoni (*Ber. R.*, **17**, 251) prepared several ethereal nitrites by the action of alcohols on amylic nitrite, and found, contrary to the experience of Röse with the carbonic ethers, that the amount of decomposition effected diminished with the increasing molecular weight of the alcohol.

It has been shown by one of us (Trans., 1885, 862; 1887, 627) that, in general, when an ethereal salt and alcohol are mixed, and a minute quantity of sodic alkylate is added, an extensive sometimes complete interchange of alkyl radicle takes place between the salt and the alcohol at the ordinary temperature. Several instances of this peculiar action of sodic alkylate noted by other observers were quoted in the paper referred to; and recently Conrad and Epstein (*Ber.*, **20**, 3057) and Peters (*Ber.*, **20**, 3323) have observed that the action is so complete in the case of mixtures of acetoacetates with alcohols, that it furnishes a convenient method of preparation from ethylic acetoacetates of other acetoacetates which are procured with difficulty by the usual methods.

The results of the experiments previously communicated by one of us to this Journal show, as might be expected, that the amount of interchange of radicle which takes place in the presence of sodic alkylate is largely influenced by the relative proportions of ethereal salt and alcohol used, but they also give some indication that the interchange is conditioned to a certain extent by the composition of the alkyl radicles concerned in the action.

Thus when sodic amylic oxide was added to a mixture of ethylic oxalate and amylic alcohol, the ethylic oxalate almost entirely disappeared and much amylic oxalate was formed, whilst in the converse case of amylic oxalate and ethylic alcohol, the formation of ethylic oxalate could not be detected. Similarly, the action between ethylic acetate and amylic alcohol, taking into account the unavoidable loss of amylic acetate incurred during fractional distillation, was apparently greater than that between amylic acetate and ethylic alcohol. The following investigation was undertaken with the view of determining

whether in general the more complex radicle may be regarded as possessing, under the conditions of our experiments, a greater affinity for the hydroxyl oxygen of the acid than the less complex radicle. Our results lead us to the conclusion that, excluding the methyl radicle, such is the case with respect at all events to acetic acid and the radicles of the C_nH_{2n+1} type.

Our experiments were conducted as follows :—

The materials were taken in the proportion of 1 mol. of ethereal salt to 1 mol. of alcohol, and $\frac{1}{100}$ atom of sodium. In each case, 50 grams of the ethereal salt were employed, and this was mixed with three-fourths of the alcohol. The sodium was dissolved in the remaining fourth, and the solution of the alkylate then added slowly to the mixture of alcohol and ethereal salt. After the mixture had stood 24 hours, it was subjected to fractional distillation, and the distillation continued until it could be inferred from the smallness of the intermediate fractions that a fairly complete separation of the low and high boiling ethereal salts had been effected. The lowest, or in some cases the two lowest boiling fractions, containing a mixture of alcohol and ethereal salt, were mixed with a measured quantity of standard potassic hydrate in excess; the mixture was allowed to stand some time in a well-stoppered flask, and then digested, using a reflux condenser until hydrolysis was complete. The residual alkali was determined by means of standard sulphuric acid, and the weight of ethereal salt in the fraction found by calculation.

In the case of the action of a low boiling alcohol on a high boiling ethereal salt, the percentage of ethereal salt which had undergone exchange of radicle was calculated directly from the amount of ethereal salt found in the low boiling fractions. In the converse case, it was impossible to determine the amount of high boiling ethereal salt formed by saponifying the higher boiling fractions, much substance being unavoidably lost from liquid left in the flask after each distillation. In these cases accordingly, the percentage of ethereal salt acted on had to be calculated from the difference between the weight of ethereal salt used and the weight of the same found in the low boiling fractions.

In every instance, a blank experiment, in which no sodic alkylate was used, was performed as far as possible under the same conditions as in the actual experiment.

As the first two experiments may be regarded as typical of the others, some details of working are given which are omitted in succeeding experiments. It may be added that in most cases, as in our second experiment, the weight of the low boiling fraction agreed to within about 1 gram with the weight calculated on the assumption that the numerical result obtained by hydrolysis represented the

actual amount of interchange of alkyl radicle that had occurred, and that the separation of the ethereal salts was complete.

*Isoamylic Acetate and Methylic Alcohol.**

Employed 50 grams of isoamylic acetate; methylic alcohol, 12·3 grams; sodium, 0·088 gram. Percentage of isoamylic acetate converted, (1) 31·7; (2) 30·7; mean 31·2. Blank experiment, 2·3. These results were obtained by hydrolysis of the fractions boiling under 70° in experiments (1) and (2), and under 70° and 70—80° in the blank experiment, after three distillations. The weights of the several fractions were as follows:—

	Experiment (2).	Blank experiment.
Under 70°	14·2	9·0
70— 80	0·6	2·0
80—100	0·5	0·8
100—120	1·0	0·5
Over 120	40·5	45·7

In experiment (2) the total weight of the two lowest boiling fractions is about 2·5 grams less than it should be on the assumption that 30·7 per cent. of the amylic acetate had been converted into methylic acetate, and it is probable therefore that the actual amount of interchange that occurred was several per cent. higher than that found, the error being due to imperfect separation of the methylic acetate from the higher boiling fractions and to loss by evaporation. It was found that in distilling 50 grams of methylic acetate an average of 0·3 gram of substance was lost during each distillation.

Methylic Acetate and Isoamylic Alcohol.

Employed methylic acetate, 50 grams; isoamylic alcohol, 59·4 grams; sodium, 0·155 gram. Percentage of methylic acetate converted, (1) 52·2; (2) 51·2; mean, 51·7. Blank experiment, 6·8.

The fractions saponified were those boiling under 70° and 70—80° after three distillations, weighing in (2) 32·5 and 2·5 grams respectively. Supposing, in this experiment, 51·2 per cent. of the methylic acetate to have been converted into amylic acetate, the mixture of residual methylic acetate with the methylic alcohol formed should weigh 35·5 grams, which agrees fairly well with the weight actually found, namely, 35 grams. The corresponding fractions in the blank experiment weighed 48·2 and 0·8 gram.

* The amyl compounds used are from ordinary fermentation amylic alcohol.

Isoamylic Acetate and Ethylic Alcohol.

Employed isoamylic acetate, 50 grams; ethylic alcohol, 17·7 grams; sodium, 0·088 gram. Percentage of isoamylic acetate converted, 25·6. Blank experiment, 4·1 per cent. These numbers were obtained by hydrolysis of the fractions boiling under 80° after six distillations.

Ethylic Acetate and Isoamylic Alcohol.

Employed ethylic acetate, 50 grams; isoamylic alcohol, 50 grams; sodium, 0·13 gram. Percentage of ethylic acetate converted, (1) 62·0; (2) 61·4; mean, 61·7. Blank experiment, 8·8. These numbers were obtained by hydrolysis of the fractions boiling in (1) and (2) under 80° after five distillations, and in the blank experiment under 85° and 85—90° after six distillations.

Isobutylic Acetate and Methylic Alcohol.

Employed isobutylic acetate, 50 grams; methylic alcohol, 13·8 grams; sodium, 0·099 gram. Percentage of isobutylic acetate converted, 42·1. Blank experiment, 8·8. The fractions saponified were those boiling under 70° and 70—80° after the distillations had been repeated four times.

Methylic Acetate and Isobutylic Alcohol.

Employed methylic acetate, 50 grams; isobutylic alcohol, 50 grams; sodium, 0·155 gram. Percentage of methylic acetate converted, (1) 45·6; (2) 44·6; mean, 45·1. Blank experiment, 6·2. The same fractions as in the last experiment were saponified.

Isobutylic Acetate and Ethylic Alcohol.

Employed isobutylic acetate, 50 grams; ethylic alcohol, 19·8 grams; sodium, 0·099 gram. Percentage of isobutylic acetate converted, 29·3; in blank experiment, 9·1. The fractions that were saponified were those boiling under 80°, 80—85°, and 85—90° after six distillations. The separation of the ethereal salt was probably less complete than in the previous experiments.

Ethylic Acetate and Isobutylic Alcohol.

Employed ethylic acetate, 50 grams; isobutylic alcohol, 42 grams; sodium, 0·13 gram. Percentage of ethylic acetate converted, 59·4; in the blank experiment, 16·1. The mixtures were distilled six times, and the fractions saponified were those boiling under 85° and 85—90°.

The separation of the residual ethylic acetate was not very satisfactory, and the numbers found are probably several per cent. too high.

Experiments similar to those described were undertaken in order to determine the amount of interaction between amylic acetate and propylic alcohol, and between propylic acetate and amylic alcohol, but from consideration of the weights of the lower boiling fractions and the results obtained by their hydrolysis, it was evident in these cases that the separation of the ethereal salts was very imperfect. With amylic acetate and propylic alcohol, the percentage numbers obtained were as follows:—Experiment with sodic alkylate, 20·9; blank experiment, 4·3; and with propylic acetate and amylic alcohol —experiment with sodic alkylate, 37; blank experiment, 32·3.

An experiment was also performed with methylic acetate, tertiary butylic alcohol, and sodic butyl oxide. The formation of butylic acetate could not be detected.

The form in which the sodic alkylate is added does not seem to have much influence on the extent of the reaction. Thus the amount of interchange of radicle occurring between methylic acetate and amylic alcohol is much the same whether the sodium be added in the form of amyl oxide or methoxide. Interchange of radicle between alcohol and ethereal salt is induced also by the addition of zinc chloride, though this substance is by no means so active as sodic alkylate.

In all the reactions we have examined, except that of propylic acetate and isoamylic alcohol, the result of which is not to be relied on, the influence of the sodic alkylate in inducing the interchange of alkyl radicle between the ethereal salt and the alcohol is very marked.

It appears further, that the extent of the interchange which occurs is not determined solely by the proportions in which ethereal salt and alcohol are present, but is influenced by the specific affinities of the alkyl radicles concerned. This is apparent from inspection of the following table, in which the experiments are arranged in pairs, so that the result of each experiment may be compared with that of its converse. In column A are given the percentages of interchange occurring when sodic alkylate is used; in column B the numbers obtained by subtracting from these the percentages found in the corresponding blank experiments. The numbers in column B represent probably more accurately, at all events in some cases, the relative amounts of interchange of alkyl radicle that take place, as by subtraction of the apparent amount of interchange occurring in the blank experiment a rough correction is applied for errors due to loss by evaporation, imperfect separation, &c.

		A.	B.
{	Isoamylic acetate and methylic alcohol ..	31·2	28·9
{	Methylic acetate and isoamylic alcohol ...	51·7	44·9
{	Isoamylic acetate and ethylic alcohol	25·6	21·5
{	Ethylic acetate and isoamylic alcohol	61·7	52·9
{	Isobutylic acetate and methylic alcohol ..	42·1	33·3
{	Methylic acetate and isobutylic alcohol ...	45·1	38·9
{	Isobutylic acetate and ethylic alcohol	29·3	20·2
{	Ethylic acetate and isobutylic alcohol	59·4	43·3

It is evident that a much greater interchange of alkyl radicle occurs when the alcohol of complex radicle acts on the ethereal salt of simple radicle than in the converse case, except in the isobutyl-methyl reactions, in which the extent of the interchange is about the same, and this holds true whether the numbers in column A or B are considered.

Experiments involving the separation of the ingredients of a complex mixture of liquids by fractional distillation are not capable of exact quantitative interpretation, and we are aware that the differences of extent of reaction shown by our numerical results may in some cases be accounted for by experimental error. We think nevertheless we are justified in drawing the conclusion that, excluding the methyl radicle, the affinity of the alkyl radicle for the hydroxyl oxygen of the acid, as measured by the special reaction under consideration, increases with increasing complexity of the alkyl radicle, but that with regard to the methyl radicle its affinity is greater than that of the ethyl, and less than that of the amyl radicle. The grounds of this conclusion will be made more evident by arranging the numerical results already given so as to show in juxtaposition the amounts of interchange which takes place when (1st) an alcohol acts on two different acetates and (2nd) two different alcohols act on one and the same acetate.

		A.	B.
1st {	Isoamylic acetate and methylic alcohol ...	31·2	28·9
{	Isobutylic acetate and methylic alcohol ..	42·1	33·3
{	Isoamylic acetate and ethylic alcohol	25·6	21·5
{	Isobutylic acetate and ethylic alcohol	29·3	20·2
{	Ethylic acetate and isobutylic alcohol	59·4	43·3
{	Methylic acetate and isobutylic alcohol ..	45·1	38·9
{	Ethylic acetate and isoamylic alcohol	61·7	52·9
{	Methylic acetate and isoamylic alcohol....	51·7	44·9
2nd {	Isoamylic alcohol and methylic acetate....	51·7	44·9
{	Isobutylic alcohol and methylic acetate ...	45·1	38·9

		A.	B.
2nd	Isoamylic alcohol and ethylic acetate	61·7	52·9
	Isobutylic alcohol and ethylic acetate	59·4	43·3
	Ethylic alcohol and isobutylic acetate	29·3	20·2
	Methylic alcohol and isobutylic acetate...	42·1	33·3
	Ethylic alcohol and isoamylic acetate	25·6	21·5
	Methylic alcohol and isoamylic acetate ...	31·2	28·9

The only numbers which do not accord with the conclusion stated above, are those given in column B for the action of ethylic alcohol on isoamylic and isobutylic acetates.

The reaction under consideration is a complex one, and its course is no doubt influenced by the relative stability of the different sodic alkylates, the etherification values of the alcohols and other factors. Menschutkin has shown that methylic alcohol holds a distinctive position among its homologues in respect of power of etherification. A similar though not identical peculiarity is also emphasised in the reaction we have studied. The power possessed by alcohols to effect interchange of alkyl radicle in presence of sodic alkylate would seem to be associated, however, with the limits and not with the initial velocity of etherification, as in correspondence with the former, excluding methylic alcohol, this power increases with increasing molecular weight of the alcohol. It may be added that our conclusions accord with the observations of Röse and of Peters already alluded to.

XXX.—*Some Interactions of Nitrogen Chlorophosphide.*

By Ward Couldridge, B.A.

Chlorophosphide of nitrogen was carefully and at length examined by Gladstone at the request of its discoverer, Liebig; and, about the same time, Gerhardt examined the interaction in which it is formed. Since that date, the only work which has been done with it, excepting Wichelhaus' confirmatory determination of its high vapour-density, is that of Hofmann, who studied the interaction of aniline and chlorophosphide of nitrogen. My object in resuming the investigation of chlorophosphide of nitrogen was, if possible, to elucidate its formation and to examine in more detail its reaction with amines. As my work proceeded, other issues suggested themselves. I endeavoured to displace the chlorine-atoms by cyanogen-groups; and as the efforts

which had been made to remove, by the action of sodium and potassium, the chlorine, and to isolate the radicle of phosphorus and nitrogen, had not given very definite results, I tried the action of zinc ethide, expecting by this means to displace the chlorine by ethyl, and thus to form compounds of which the reduction products would have been interesting. But to work with this substance one has to meet the difficulty of its preparation, and as Gladstone found the yield is but small.

My method of preparation was a slight modification of that given by Gladstone (*Jour. Chem. Soc.*, **3**, 135). Instead of attaching receivers directly to the flask in which the ammonium chloride and the phosphorus pentachloride are heated by a Bunsen burner, a straight condenser was first fixed to the flask in order to return to the sphere of action any unaltered vaporised pentachloride, and to condense the chlorophosphide of nitrogen, which would otherwise have been carried over by the evolved hydrogen chloride, and would, in part, have been lost. The chlorophosphide of nitrogen was purified by driving over with steam. The objection to this method of purification is that the steam decomposes some of the product; but in its favour is the fact that it is less trouble than to extract with anhydrous ether. The yield was somewhat variable; but in no case was it large. The maximum yields I obtained amounted to 10 grams of chlorophosphide of nitrogen from 100 grams of phosphorus pentachloride and 200 grams of ammonium chloride; whereas the theoretical yield calculated from the equation—

$$3PCl_5 + 3NH_3 = P_3N_3Cl_6 + 9HCl,$$

would be 41 grams. Gladstone states that his yield was uniformly about 6 per cent. of the pentachloride used.

The smallness of the yield is most probably explained by the following experiments. I found that when dry ammonia gas is passed through a dry tube over melted chlorophosphide of nitrogen, a reaction takes place, which results in the transformation of the greater part of the latter substance into a greyish-white infusible powder, and in the volatilisation of the smaller portion on to the cooler part of the tube, where it remains unaltered; this same greyish-white infusible substance is also obtained when chlorophosphide of nitrogen and ammonium chloride are heated in a sealed tube at a temperature of 150° for an hour or more; at the end of which time mere traces only of chlorophosphide of nitrogen remain. The following equation represents the reaction:—

$$P_3N_3Cl_6 + 3NH_3 = \underset{\text{Phospham.}}{P_3N_3(NH)_3} + 6HCl.$$

The greyish-white infusible substance is readily characterised as phospham. This easy transformation of chlorophosphide of nitrogen into phospham renders the view distinct that the molecule of phospham is not $PN(NH)$ but is $P_3N_3(NH)_3$, just as chlorophosphide of nitrogen is not $PNCl_2$ but is $P_3N_3Cl_6$.

The production in the first instance of chlorophosphide of nitrogen receives a simple explanation in terms of the following equation :—

$$\begin{matrix} Cl \\ Cl \\ Cl \end{matrix}\!\!>\!PCl + 3\begin{matrix} H \\ H \\ N \end{matrix}\!\!> = P_3N_3Cl_6 + 9HCl.$$

Gerhardt (*Ann. Chim. Phys.*, **18**, 205), who investigated the action of phosphorus pentachloride on ammonium chloride, concluded that the formation of phosphorus nitrogen chloride,* occurring as it does in small quantities, was accidental. But the above-mentioned action of ammonia would lead to another conclusion. And, indeed, not only does ammonia react with phosphorus nitrogen chloride, but also amines generally appear to remove the chlorine. Hofmann (*Ber.*, **17**, 1909) found that by dissolving phosphorus nitrogen chloride in aniline, and warming the solution on a water-bath, the whole solidified; and from the solid mass, by extracting the aniline hydrochloride and the unaltered aniline by hydrochloric acid and water, he obtained a white, solid substance, which, after crystallisation from glacial acetic acid, gave on analysis numbers corresponding to the constitution

$$P_3N_3(NH{\cdot}C_6H_5)_6.$$

I repeated this experiment, using somewhat larger quantities of substances. There was formed the white substance which Hofmann described, and together with it a viscid dark-coloured oil, which was separated by digestion with cold alcohol, after treating the solid mass with hydrochloric acid and water. This oily substance is extremely soluble in alcohol, ether, and benzene, and appears to be unaltered by boiling with a large quantity of water for 10 hours. All attempts to crystallise it were futile; and after standing for two months it shows no signs of crystallisation. This resinous matter was formed in every case from the action of phosphorus nitrogen chloride on the amines which I used.

Hofmann considered that if this compound, $P_3N_3(NH{\cdot}C_6H_5)_6$, were heated with hydrochloric acid, it might lose 3 mols. of aniline and be converted into the corresponding phospham-derivative, $P_3N_3(NC_6H_5)_3$. But I found that when heated in a sealed tube with strong hydrochloric acid, it remained unaltered at a temperature of 150°, and

* This name seems preferable to "chlorophosphide of nitrogen."

when the temperature was raised to 250°, it was completely decomposed into phosphoric acid, ammonium chloride, and aniline. Thus—

$$P_3N_3(NH\cdot C_6H_5)_6 + 12H_2O + 9HCl = 3NH_4Cl + 6C_6H_5\cdot NH_2,HCl + 3H_3PO_4.$$

I next used, instead of aniline, orthotoluidine. On mixing together the phosphorus nitrogen chloride and the orthotoluidine the mixture gets warm; and on heating on the water-bath it finally solidifies. Instead of at first treating the solid mass with hydrochloric acid, I used ether to remove the excess of orthotoluidine, fearing lest the hydrochloric acid might be the cause of the production of the resinous substance. After filtering off the ethereal extract, a white solid remained, but its ready solubility in water proved it to be orthotoluidine hydrochloride. The ethereal extract gave a residue, after the removal of the free orthotoluidine, of a viscid oil, similar to that obtained when aniline was used. Thus at 100°, no product of the type $P_3N_3R_6$ was formed. But when the orthotoluidine and the phosphorus nitrogen chloride were heated at temperatures of 150° or 250°, such a substance was produced together with the resin; so that on extracting the solid mass with ether, and with hydrochloric acid and water, a white substance remained, which could be crystallised in slender needles from hot alcohol. Its melting point is 241—242°. The formula $P_3N_3(NH\cdot C_6H_4\cdot CH_3)_6$ requires 12·17 per cent. of nitrogen; I found 12·16.

When phenylhydrazine was used, there was, at a temperature of 100°, formed in addition to the viscid oil, a crystallisable substance which I extracted as in the previous instance. It was crystallised from alcohol. Its melting point was 200°. The constitution, $P_3N_3(NH\cdot NH\cdot C_6H_5)_6$, requires 11·97 per cent. of phosphorus and 27·03 per cent. of nitrogen; my analysis gave 12·15 per cent. of phosphorus and of nitrogen 27·27.

The reaction with piperidine and phosphorus nitrogen chloride is very rapid. So much heat is evolved that the piperidine begins to boil. The reaction is completed by warming on a water-bath. The products are here again a viscid oil, in much smaller quantity than in the other instances, and a crystallisable compound. The latter can with difficulty be crystallised from alcohol. On heating, it decomposed before melting.

The formula $P_3N_3(NC_5H_{10})_6$ would require—

		Found.
Phosphorus	14·08 per cent.	14·3
Nitrogen	19·89 „	19·8

Diphenylamine and diamylamine do not at ordinary temperatures react with phosphorus nitrogen chloride.

Attempts were made to prepare cyanogen-derivatives of phosphorus nitrogen chloride by dissolving it in alcohol and heating the solution with silver cyanide at a 100° for several hours. But the phosphorus nitrogen chloride was entirely decomposed, and prussic acid was set free. On evaporating the alcohol a thick oil with a strongly acid reaction was obtained. It readily gave off ammonia when warmed with baryta-water, and otherwise reacted as a mixture of acid ammonium salts. It showed Gladstone's test for azophosphoric acid; for on adding a drop of ferric chloride to the ammoniacal solution of the acid, the liquid became brown, and no trace of precipitate was formed. But on applying this test to a solution of ammonium phosphate, I obtained exactly the same result.

Previous efforts which had been made to remove the chlorine and to isolate the radicle had not yielded very definite results. I found that sodium or sodium amalgam acts very slowly on a benzene solution of phosphoric nitrogen chloride; so I mixed it with dry zinc-dust, exhausted the tube, and heated the mixture. Much gas was evolved smelling of cyanogen. The phosphorus nitrogen chloride was entirely decomposed, and the phosphorus remained behind in combination with the zinc. I next tried the action of zinc ethide on the phosphorus nitrogen chloride; but at ordinary temperatures the substances do not react.

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XXXI.—*Action of Phosphorus Pentachloride on Salicylaldehyde.*

By Charles M. Stuart, M.A., Fellow of St. John's College, Cambridge.

It is stated by Henry (*Ber.*, **2**, 135) that the action of phosphorus pentachloride on salicylaldehyde first produces dichlororthocresol, $CCl_2H{\cdot}C_6H_4{\cdot}OH$, but that the further action of the pentachloride displaces the hydroxyl-group by chlorine, giving rise to orthochlorobenzalchloride, $C_6H_4Cl{\cdot}CCl_2H$; by the action of water on this at 170°, orthochlorobenzaldehyde, $C_6H_4Cl{\cdot}COH$, may be prepared. (See *Watts' Dictionary*, **8**, 302.)

On attempting to prepare orthochlorobenzaldehyde in this way, I found that if the mixture of phosphorus pentachloride and salicyl-

aldehyde was heated, it was entirely carbonised, whilst if it were poured into water the product always contained phosphorus; I therefore undertook a more complete examination of this reaction.

Salicylaldehyde was added to phosphorus pentachloride in molecular proportion, care being taken to keep the mixture cool; on pouring the product into water, the water became heated by the decomposition of the phosphorus oxychloride, and a pink oil separated; on cooling, this became semi-solid, and after being washed with potash and crystallised from alcohol, it formed tufts of white needles melting at 78°.

On analysis—

0·4944 gram gave 0·0984 gram $Mg_2P_2O_7$.
0·4058 „ 0·6518 „ CO_2.
0·1014 „ H_2O.

0·5287 gram required 54·95 c.c. $\frac{n}{10}$ $AgNO_3$ sol.,

corresponding to—

		Theory for $C_{21}H_{15}Cl_6PO_4$.
C	43·80	43·74
H	2·77	2·61
P	5·55	5·37
Cl	36·89	37·06

Its constitutional formula is $PO(O{\cdot}C_6H_4{\cdot}CCl_2H)_3$. The first action of phosphorus pentachloride is to displace the oxygen of the COH-group by Cl_2 giving dichlororthocresol, but this is at once acted on by the phosphorus oxychloride produced, this reaction taking place according to the equation—

$$POCl_3 + 3C_6H_4(HO){\cdot}COH = PO(O{\cdot}C_6H_4{\cdot}CCl_2H)_3 + 3HCl.$$

In this way, phosphate of dichlororthocresol is formed, just as triphenyl phosphate is by the action of phosphorus pentachloride on phenol.

Phosphate of dichlororthocresol is not altered by boiling with a 10 per cent. solution of caustic potash; and even with a saturated solution it is not entirely decomposed, the solution containing a little chloride and phosphate only.

On treating its alcoholic solution with alcoholic potash, however, potassium chloride at once separates, but no phosphate was obtained on boiling. In this respect it resembles triphenyl phosphate, which is not saponified by boiling with potash.

It now seemed of interest to ascertain what would take place in this reaction if the hydrogen of the hydroxyl-group were already dis-

placed by some radicle, and for this purpose methyl salicylaldehyde was chosen.

Methyl salicylaldehyde was added to phosphorus pentachloride in molecular proportion; the phosphorus oxychloride produced was distilled off under diminished pressure, and the residue shaken up with ether and a solution of acid sodium sulphite; the ethereal solution was then dried with calcium chloride, and the ether distilled off; the residual oil distilled at 231°. On analysis 0·3285 gram gave 0·6065 gram CO_2 and 0·1179 gram H_2O.

	Found.	Theory. $C_8H_8OCl_2$.
C	50·33	50·26
H	3·98	4·18

It is therefore orthomethoxybenzalchloride, $C_6H_4(OCH_3)\cdot CCl_2H$, produced by the displacement of the oxygen of the COH-group in methyl salicylaldehyde by Cl_2. It is extremely unstable, and is at once decomposed by warm water, yielding methyl salicylaldehyde; it decomposes slowly in moist air, and in preparing it any rise of temperature or prolonged contact with water must be avoided. I think it worth remarking that when the hydroxylic hydrogen of dichlor-orthocresol is displaced by methyl, the CCl_2H-group is decomposed by water, whereas if the same hydrogen is displaced by phosphoric acid, the CCl_2H-group is not altered by boiling with potash.

XXXII.—*Researches on Chrom-organic Acids.* Part II. *Certain Chromoxalates. Red Series.*

By Emil A. Werner, Assistant in the Chemical Laboratory, Trinity College, University of Dublin.

The first member of the red series of chromoxalates was discovered by Crofts in 1842 (*Phil. Mag.*, **21**, 197), but has hitherto been little studied. Salts of this series are in all cases constant products of the reduction of dichromates by oxalic acid, the compounds of the blue series, which are formed under conditions described in the first part of this paper (Trans., **51**, 383), being the result of the direct addition of oxalic acid or an oxalate to the red salt.

Regarded as anhydrous compounds, the salts of the blue and red series are represented respectively by the formulæ $M'_6Cr_2(C_2O_4)_6$ and $M'_2Cr_2(C_2O_4)_4$.

The potassium salt was prepared by the interaction of potassium dichromate (1 mol.) and oxalic acid (7 mols.), both in aqueous solution; the composition of the purple-red crystals which separate from the concentrated liquid, and to which Crofts assigned the formula $K_2Cr_2(C_2O_4)_4,12H_2O$, I find to be correctly represented by the formula $K_2Cr_2(C_2O_4)_4,10H_2O$. The method of analysis was the same as that adopted in the case of the blue chromoxalates.

		Found.	
	Theory.	I.	II.
K_2	10·92 p. c.	11·08 p. c.	11·26 p. c.
Cr_2	14·56 „	14·19 „	14·34 „
$(C_2O_4)_4$.....	49·29 „	49·17 „	49·21 „
$(H_2O)_{10}$	25·21 „	22·72 „	25·19 (by diff.).
	99·98	97·06	100·00

The apparent deficiency in the water-determination of the first analysis—the result of direct experiment—is due to the fact that the last 2 mols. H_2O in this salt are only expelled at an exceptionally high temperature. The behaviour of the water in this salt has such an important bearing on its constitution, that I append the experimental results obtained during the dehydration of the compound.

Weight taken, 1·153 gram.

	Time.		H_2O.	Molecules.
Heated to 110—120° C.	2 hrs.	Loss = 0·1865 gram	= 16·17	6·33
„ „	4 hrs.	„ = 0·1865 „	= „	„
„ 150°	2 hrs.	No further loss	—	—
„ 180	2 hrs.	Loss = 0·2145 gram	= 18·60	7·37
„ „	4 hrs.	„ = 0·2255 „	= 19·55	7·74
„ 180—200° C.	2 hrs.	„ = 0·2415 „	= 20·94	8·29
„ 200—225	2 hrs.	„ = 0·2535 „	= 21·98	8·70
„ „	4 hrs.	„ = 0·2621 „	= 22·72	8·99

The loss of the first 6 mols. H_2O is accompanied by a change of colour from red to bluish-grey, and after 8 mols. have been lost the salt commences to become green; at the time that the above analyses were made, the appearance of the latter colour was thought to be due to decomposition, but I have since found that the salt may be heated to a temperature approaching 300° without decomposition. 0·243 gram heated cautiously until the whole mass assumed a deep green colour lost 0·062 gram = 25·51 per cent. of total water. Calc. 25·21 per cent.

When strongly ignited with access of air, this compound leaves a

residue of chromic oxide and potassium chromate, the decomposition taking place according to the equation—

$$2K_2Cr_2(C_2O_4)_4,10H_2O + 11O = 2K_2CrO_4 + Cr_2O_3 + 10H_2O + 16CO_2.$$

which represents a residue = 37·81 per cent., or 36 per cent. if the salt contained $12H_2O$; 0·4897 gram left residue = 0·1848 gram, corresponding with 37·72 per cent. My formula, therefore, is the correct one.

When the decahydrated salt is exposed over sulphuric acid in a desiccator, it continues to lose water for several weeks, but the loss ceases when the compound has the composition $K_2Cr_2(C_2O_4)_4,4H_2O$. This also represents the composition of the salt dried at 110—120°; if, however, the aqueous solution of the salt is evaporated to dryness on the water-bath, it leaves a green amorphous residue which has the composition $K_2Cr_2(C_2O_4)_4,2H_2O$.

Crofts considered this compound to be a double salt of potassium oxalate and chromic oxalate, thus: $K_2C_2O_4 + Cr_2(C_2O_4)_3$, differing simply from Gregory's compound by 2 mols. $K_2C_2O_4$, since on boiling its solution with the latter, Gregory's blue salt is produced, thus:—

$$K_2Cr_2(C_2O_4)_4 + 2K_2C_2O_4 = K_6Cr_2(C_2O_4)_6.$$

This view of the constitution of these salts, as I have already pointed out, is quite untenable, and its inconsistency with their peculiar properties is particularly recognised in this somewhat remarkable compound.

With the exception that their solutions are not precipitated by either calcic chloride or ammonia, the salts of the red series differ remarkably in their properties from the blue; they do not yield corresponding salts by double decomposition. The only other compounds of the series hitherto described are the complete sodium and ammonium salts (Warington, *Phil. Mag.*, **21**, 202). I have succeeded in producing the potassium ammonium compound,

$$K(NH_4)Cr_2(C_2O_4)_4,10H_2O,$$

by the following reaction:—

$$KNH_4Cr_2O_7 + 7H_2C_2O_4 = K(NH_4)Cr_2(C_2O_4)_4 + 6CO_2 + 7H_2O.$$

This salt is of interest in proving that the simplest formula for these compounds must contain at least 2 atoms of chromium. This compound forms small purple-red monoclinic prisms; they are more freely soluble in water than the potassium salt itself, which in every other respect they resemble closely.

A remarkable property of the salts of this series is the readiness

with which they form addition products. With ammonium oxalate Croft's salt yields the compound $K_2(NH_4)_4,Cr_2(C_2O_4)_6,6H_2O$; it also combines with the oxalates of the different types of organic bases, yielding in some cases beautifully crystallised compounds. The combinations of these red salts are not restricted to oxalates, but extend also to salts of certain other organic acids, yielding in each case products in which the new acid radicle can no longer be detected by the usual reagents. These compounds will be described in another paper.

The effect of alkalis, and particularly of ammonia, on the red salt is very peculiar: if to the rich red solution of the latter an alkali be added, the colour of the liquid will immediately change to green; on adding an acid in excess the original red colour of the liquid is restored. This colour change is very delicate, the green solution being sensitive even to carbonic acid. In the case of the fixed alkalis, decomposition of the green liquid, with separation of chromic hydroxide, takes place after 5 to 6 mols. of alkali have been added for each mol. of the red salt. In an experiment, 7·14 grams of the red salt required at the boiling temperature 2·20 grams NaOH for decomposition, corresponding to 5·5 mols. This behaviour with alkali seemed entirely in favour of a view regarding the constitution of the red salt, which had already been suggested to me by Dr. Emerson Reynolds, on his consideration of my results obtained on heating the compound to the very high temperature at which it lost the last 2 mols. of H_2O; namely, that in this compound there were *at least* two, but more probably four, hydroxyl-groups in the molecule. Looking upon it as a derivative of chromic hydroxide, the constitution of Croft's salt may be expressed by the following structural formula:—

$$\begin{matrix} OK\cdot C_2O_2\cdot O \\ OH\cdot C_2O_2\cdot O \end{matrix}\!\!>\!(OH)Cr\cdot Cr(OH)\!<\!\begin{matrix} O\cdot C_2O_2\cdot OK \\ O\cdot C_2O_2\cdot OH \end{matrix} = K_2H_2Cr_2(C_2O_4)_4(OH)_2.$$

in which the hydrogen-atoms of four of the hydroxyls have been displaced. According to this formula, the compounds would contain the hydroxyls in two distinct positions, whereby two would be basic and two acidic, tending to neutralisation; as a matter of fact the acidic property predominates in the red salt, as the feeble basic powers of chromic hydroxide would naturally indicate.

The existence of the compound $K_4Cr_2(C_2O_4)_4(OH)_2$, obtained in the following way, is strong evidence in favour of the above constitution ascribed to the red salt. A quantity of the latter in aqueous solution was mixed with 2 mols. of caustic potash, and the greenish-red solution precipitated with alcohol; the mixture was then warmed on the water-bath, which caused the precipitate to quickly coagulate and attach itself to the sides and bottom of the flask, from which, after

decanting the mother-liquor and heating in the air-bath, it was easily removed.

When dry, it forms a dull greenish-red dichroic powder, which on heating at 110° to expel H_2O gave the following results on analysis:—

0·3854 gram gave 0·091 gram Cr_2O_3.
0·3854 gram gave 0·206 gram K_2SO_4.
(I) 0·346 gram gave 0·188 gram (C_2O_4); (II) 0·441 gram gave 0·2399 gram (C_2O_4).

From which the following percentage composition is obtained.

	Theory.	Found. I.	Found. II.
K_4.....	24·14 p. c.	24·00 p. c.	—
Cr_2	16·10 „	16·22 „	—
$(C_2O_4)_4$....	54·48 „	54·39 „	54·42 p. c.
$(OH)_2$	5·26 „	5·39 (by diff.)	—
	99·98	100·00	

This compound, as indicated by its constitution, possesses a feeble *alkaline* reaction.

When ignited, it leaves a residue of potassium chromate, the decomposition taking place according to the equation—

$$K_4Cr_2(C_2O_4)_4(OH)_2 + 7O = 2K_2CrO_4 + 8CO_2 + H_2O,$$

which requires a residue = 60·06 per cent.; 0·3854 gram ignited with free access of air left a residue = 0·231 gram, corresponding to 59·93 per cent. Heated to a temperature approaching 300°, this compound loses its reddish tint, leaving a pure green residue of the corresponding anhydride, thus:—

$$\begin{matrix}(OH)Cr(O\cdot C_2O_2\cdot OK)_2\\ |\\ (OH)Cr(O\cdot C_2O_2\cdot OK)_2\end{matrix} = O\begin{matrix}<Cr(O\cdot C_2O_2\cdot OK)_2\\ |\\ >Cr(O\cdot C_2O_2\cdot OK)_2\end{matrix} + H_2O.$$

In the same way the original red salt near 300° yields its corresponding anhydride by loss of 2 mols. H_2O.

$$\begin{matrix}OK\cdot C_2O_2\cdot O\cdot Cr<\begin{matrix}O\cdot C_2O_2\cdot OH\\ OH\end{matrix}\\ |\\ OK\cdot C_2O_2\cdot O\cdot Cr<\begin{matrix}OH\\ O\cdot C_2O_2\cdot OH\end{matrix}\end{matrix} = \begin{matrix}OK\cdot C_2O_2\cdot O\cdot Cr<\begin{matrix}O\\ O\end{matrix}>C_2O_2\\ |\\ OK\cdot C_2O_2\cdot O\cdot Cr<\begin{matrix}O\\ O\end{matrix}>C_2O_2\end{matrix} + 2H_2O.$$

With ammonia, the chromoxalates of the red series react in a peculiar manner; when it is added to the red solution of the potash salt,

a deep-green liquid is formed, as in the case of the fixed alkalis, and when all free ammonia has been expelled by boiling, 2 mols. are still retained for each mol. of red salt employed corresponding to the compound $K_2(NH_4)_2Cr_2(C_2O_4)_4$. If ammonia gas be passed to saturation into the green solution, or better if the finely-powdered red salt be treated with strong aqueous ammonia, it dissolves after a short time, yielding an intense claret-coloured liquid which on boiling becomes green. Alcohol added in excess to the red ammoniacal liquid, throws down a dull red crystalline precipitate which, after drying by a gentle heat, gave results on analysis which lead to the formula $K_2Cr_2(C_2O)_4),6NH_3,6H_2O$.

(I) 0·4535 gram gave 0·0629 gram NH_3; (II) 0·324 gram gave 0·045 gram NH_3.

0·328 gram gave 0·15417 gram (C_2O_4) radicle.

(I) 0·3472 gram gave 0·0865 gram K_2SO_4; (II) 0·3175 gram gave 0·0774 K_2SO_4.

0·3175 gram gave 0·0636 gram Cr_2O_3.

Calculated percentage composition:—

		Found.	
	Theory.	I.	II.
K_2	10·48 p. c.	11·04 p. c.	10·82 p. c.
Cr_2.....	13·97 „	13·75 „	—
$(C_2O_4)_4$	47·31 „	47·00 „	—
$(NH_3)_6$	13·71 „	13·87 „	13·88 „
$(H_2O)_6$	14·51 „	14·34 (by diff.)	—
	99·98	100·00	

It readily loses ammonia on heating.

When ignited, it leaves a residue of potassium chromate and chromic oxide thus:—

$$2K_2Cr_2(C_2O_4)_4,6NH_3,6H_2O + 13O = 2K_2CrO_4 + Cr_2O_3 + 16CO_2 + 12NH_3 + 12H_2O,$$

corresponding to 36·29 per cent.; 0·1715 gram left a residue weighing 0·063 gram = 36·67 per cent.

If the salt $(NH_4)_2H_2Cr_2(C_2O_4)_4(OH)_2$* be treated with ammonia solution, in place of Croft's salt, alcohol precipitates the compound $Cr_2(C_2O_4)_4,6NH_3,6H_2O$; as deduced from the following analysis:—

* Warington's ammonium salt represented as a hydroxyl compound.

0·2372 gram gave 0·0546 gram Cr_2O_3; 0·2267 gram gave 0·0351 gram NH_3.

0·396 gram gave 0·2087 gram (C_2O_4) radicle.

	Theory.	Found.
$(NH_3)_6$.....	15·31 p. c.	15·49 p. c.
Cr_2	15·61 „	15·81 „
$(C_2O_4)_4$.....	52·85 „	52·77 „
$(H_2O)_6$.....	16·21 „	15·93 (by diff.)
	99·98	100·00

When heated, this compound readily loses part of its ammonia. On ignition it leaves a residue of chromic oxide; 0·2372 gram left a residue weighing 0·0546 gram = 23·01 per cent. Theory 22·82 per cent.

The addition of calcic chloride to solutions of these compounds produces an immediate precipitate of calcium oxalate; hydrochloric acid added to warm concentrated solutions causes the separation of oxalic acid on cooling, together with small red crystals of the corresponding chloride. From these reactions, it will be seen that these two compounds are no longer chromoxalates, but appear to be the oxalates of a peculiar class of chromammonium base.

In an experiment with a view to displace the two hydroxylic hydrogen-atoms in the compound $K_4Cr_2(C_2O_4)_4(OH)_2$ by potassium, by the direct action of potash (4 mols.) on the red salt, and precipitation of the solution with alcohol, a compound was obtained belonging to a new class of chromoxalates containing 4 atoms of chromium in the molecule, apparently resulting from the condensation of 2 mols. of the di-hydroxyl compound with elimination of oxalic acid. The nature of this reaction has not yet been sufficiently studied for interpretation, and is being investigated.

I here take the opportunity of acknowledging the receipt of a paper from Professor F. W. Clarke, containing a communication made to the American Chemical Society some years ago, on the *blue* series of chromoxalates. In this paper, Professor Clarke has assigned to these compounds a constitution similar to that independently adopted by me in my former paper. Professor Clarke's paper completely escaped my notice at the time.

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XXXIII.—*The Action of Isothiocyanates on the Aldehyde-ammonias.*

By Aug. E. Dixon, M.D., Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

Acetaldehyde-ammonia is known to combine with certain of the "mustard-oils;" thus, R. Schiff (*Ber.*, **9**, 565) has described compounds obtained by the action of the former on ethyl-, allyl-, and phenyl-thiocarbimides respectively.

Some time ago, happening to have in my possession a quantity of benzylthiocarbimide, I tried its action on acetaldehyde-ammonia; with the result that the two substances readily combined under the following conditions:—

1 mol. of benzylthiocarbimide, dissolved in a small quantity of strong alcohol, was mixed with a concentrated alcoholic solution of 2 mols. of aldehyde-ammonia. The mixture was gently warmed on the water-bath, and in a few minutes solid matter began to separate; on removing the dish from the water-bath, the contents almost immediately set to a white crystalline mass. This was drained on the filter-pump, and pressed between filter-paper. It was then shaken up with cold spirit, and again drained and pressed. On carefully recrystallising the product from hot absolute alcohol, a woolly mass of white, shining needles was obtained, which was dried over sulphuric acid under the air-pump receiver.

The substance is sparingly soluble in cold alcohol; it dissolves tolerably freely in boiling alcohol, by which, however, it is gradually decomposed, with evolution of ammonia and aldehyde. It is insoluble in water, sparingly soluble in ether and bisulphide of carbon, more easily in chloroform. Benzene when hot dissolves it moderately, but when cold very sparingly. It melts at 175° with browning and copious evolution of gas. The alcoholic solution is slowly desulphurised by boiling with alkaline lead tartrate;* with excess of silver nitrate a white precipitate separates, which on standing quickly blackens. Ammoniacal silver nitrate gives a yellow precipitate which blackens on boiling.

The substance was found to contain carbon, hydrogen, nitrogen, and sulphur.

On analysis, the following data were obtained:—

0·2192 gram burnt with lead chromate gave 0·1507 H_2O and 0·4966 CO_2,

or C = 61·78, H = 7·66.

* Described by Emerson Reynolds, Trans., 1884, 162.

0·2230 gram gave 0·5042 CO_2 (hydrogen lost),
or C = 61·65.

0·3344 gram burnt with soda-lime gave 0·4208 Pt,
or N = 18·13 per cent.

0·2492 gram fused with Na_2CO_3 + $KClO_3$ gave 0·2358 $BaSO_4$,
or S = 13·01 per cent.,

from which the formula $C_{12}H_{17}N_3S$ is deduced.

			Theory.	Experiment.			
				I.	II.	III.	IV.
C_{12}	143·64	.....	61·21	61·78	61·65	—	—
H_{17}	17·00	.....	7·24	7·66	—	—	—
N_3	42·03	.....	17·91	—	—	18·13	—
S	31·98	.....	13·62	—	—	—	13·01
	234·65		99·98	—	—	—	—

The reaction may be represented thus:—

$$C_7H_7{\cdot}NCS + 2C_2H_4O,NH_3 = C_{12}H_{17}N_3S + 2H_2O.$$

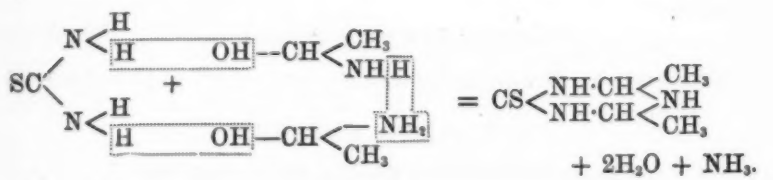
This decomposition recalls the observation made by Nencki (*Ber.*, **7**, 162), that thiocarbamide and aldehyde-ammonia unite, with elimination of water and NH_3:—

$$CS(NH_2)_2 + 2C_2H_4O,NH_3 = C_5H_{11}N_3S + NH_3 + H_2O.$$

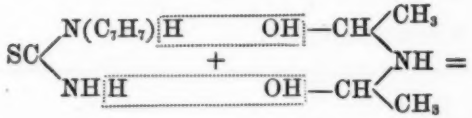
Nencki considers the compound $C_5H_{11}N_3S$ to be an ammonia-derivative of diethylidenethiocarbamide, $CS(N:C_2H_4)_2$, and writes its formula—

$$\left.\begin{matrix} CS \\ C_2H_4 \\ C_2H_4 \end{matrix}\right\} N_2,NH_3.$$

From the mode of formation of this compound, we may suppose the $SC{<}\begin{matrix}N\\N\end{matrix}{<}$ group to exist in it; and the decomposition may be represented thus:—



We may suppose, now, that in the case of benzylthiocarbimide, the NH_3, which 2 mols. of aldehyde-ammonia can afford (as above), instead of being evolved, is fixed by the thiocarbimide, forming, perhaps, for the moment, benzylthiocarbamide, which then reacts with the aldehyde-ammonia residue—



$$SC\begin{cases} N(C_7H_7)H \\ NH \end{cases} + \begin{matrix} OH-CH\begin{cases} CH_3 \\ NH \end{cases} \\ H \qquad\quad OH-CH\begin{cases} CH_3 \end{cases} \end{matrix} =$$

$$SC\begin{cases} N(C_7H_7)CH\begin{cases} CH_3 \\ NH \end{cases} \\ NH-CH\begin{cases} CH_3 \end{cases} \end{cases} + 2H_2O.$$

Thus the compound of benzylthiocarbimide with aldehyde-ammonia would be a benzylated derivative of Nencki's "*Diäthylidenthioharnstoffammoniak.*"

The first question now was—can homologues of methyl be substituted for the *methyl*-groups? The answer was obtained as follows:—

1 mol. benzylthiocarbimide, dissolved in spirit, was added to a spirituous solution containing 2 mols. of ordinary (hydrated) isovaleraldehyde-ammonia. Crystals soon began to separate, and the mixture was exposed freely to the air (at ordinary temperature) till most of the liquid had evaporated. The crystalline mass was drained, and pressed on the filter-pump, washed lightly with spirit, and dissolved in hot absolute alcohol. The latter somewhat decomposed the substance,—valeraldehyde and ammonia being evolved,—but, on cooling, beautiful, snow-white, silky needles separated, forming a felted mass which retained much mother-liquor. It was thrown on the filter-pump, washed repeatedly with cold alcohol, and dried over sulphuric acid in a vacuum.

The substance is insoluble in water, soluble easily in hot, sparingly in cold alcohol, soluble in chloroform, ether, and bisulphide of carbon, and easily soluble in warm benzene. It melts at 161—162° with decomposition. Silver nitrate gives a finely granular, white precipitate, which blackens gradually on standing, or instantly on addition of ammonia. The alcoholic solution is slowly desulphurised by boiling with alkaline lead solution.

The following data were obtained on analysis:—

0·2313 gram, burnt with lead chromate, gave 0·5764 CO_2 and 0·1932 H_2O,

or C = 67·96 per cent.; H = 9·28 per cent.

0·2264 gram gave 0·5639 CO_2 and 0·1875 H_2O,

or C = 67·92 per cent.; H = 9·20 per cent.

0·2564 gram, burnt with copper oxide, gave 29 c.c. N at 9° C. and 755 mm.,

or 13·50 per cent. N.

0·3042 gram, evaporated to dryness with sodium hydrate in a nickel crucible and fused with potassium nitrate,* gave 0·2170 $BaSO_4$,

or S = 9·80 per cent.,

which agrees with the formula $C_{18}H_{29}N_3S$.

			Theory.	Experiment.			
				I.	II.	III.	IV.
C_{18}	215·46	.....	67·65	67·96	67·92	—	—
H_{29}	29·00	.....	9·10	9·28	9·20	—	—
N_3	42·03	.....	13·19	—	—	13·50	—
S	31·98	.....	10·04	—	—	—	9·80
	318·47		—	—	—	—	—

The reaction may be represented thus :—

$$C_7H_7{\cdot}NCS + 2CH(CH_3)_2{\cdot}CH_2{\cdot}COH,NH_3 = C_{18}H_{29}N_3S + 2H_2O,$$

and the provisional formula ascribed is—

$$SC\begin{matrix}<^{N(C_7H_7){\cdot}CH<^{C_4H_9}_{NH}}\\ <_{NH}\end{matrix}\!\!-\!\!-CH<^{C_4H_9}_{NH}.$$

This compound is accordingly homologous with that previously described, butyl-groups being substituted for the methyl-groups.

The next question was: Can other radicles be substituted for the benzyl-group? To this an affirmative answer was also obtained.

(*a.*) *Ethylthiocarbimide and Aldehyde-ammonia.*†

Warm, concentrated alcoholic solutions of ethylthiocarbimide (1 mol.) and aldehyde-ammonia (2 mols.) were mixed. On cooling, crystals separated, which were collected and pressed. After two recrystallisations from spirit, they were found to melt—though not without decomposition—at 135—136°. At a few degrees higher they decompose completely, with evolution of gas.

* This is the method now regularly used by Professor Reynolds for the determination of sulphur (and halogens) in suitable thio-compounds; it gives very satisfactory results. The details will probably be published shortly.

† By the action of aldehyde-ammonia on ethylthiocarbimide, R. Schiff obtained results which will be referred to later on.

Analytical data:—

0·2419 gram, burnt with lead chromate, gave 0·4315 CO_2 and 0·1911 H_2O,

or C = 48·64; H = 8·77.

0·2534 gram, burnt with copper oxide, gave 54·1 c.c. N at 10° C. and 742 mm.,

or N = 24·94 per cent.

0·3394 gram, evaporated to dryness with sodium hydrate solution and fused with nitre, gave 0·4484 gram $BaSO_4$,

or S = 18·16 per cent.

This agrees with the formula $C_7H_{15}N_3S$.

		Theory.	Experiment.		
			I.	II.	III.
C_7	83·79	48·49	48·64	—	—
H_{15}	15·00	8·68	8·77	—	—
N_3	42·03	24·32	—	24·94	—
S	31·98	18·50	—	—	18·16
	172·80	—	—	—	—

The structural formula may be provisionally written—

$$SC<\begin{matrix}N(C_2H_5)\cdot CH<CH_3\\ NH\text{——}CH<NH\\ \qquad\qquad\quad CH_3\end{matrix}.$$

*Allylthiocarbimide and Aldehyde-ammonia.**

The allyl compound was prepared similarly to the preceding. It formed white woolly masses of needles, which after two recrystallisations from spirit, melted at 108—109°.

Analytical data:—

0·2057 gram, burnt with lead chromate, gave 0·3913 CO_2 and 0·1621 H_2O,

or C = 51·87; H = 8·75.

0·2465 gram, burnt with copper oxide, gave 47·6 c.c. N at 12° C. and 767 mm.,

or N = 23·13 per cent.

* See note under ethylthiocarbimide; *ante*.

0·1423 gram, evaporated to dryness with sodium hydrate solution, and fused with nitre, gave 0·1820 $BaSO_4$

or S = 17·58 per cent.,

from which the formula $C_8H_{15}N_3S$ is deduced.

		Theory.	Experiment.		
			I.	II.	III.
C_8	95·76	51·83	51·87	—	—
H_{15}	15·00	8·11	8·75	—	—
N_3	42·03	22·75	—	23·13	—
S	31·98	17·30	—	—	17·58

which may be represented—

$$SC<\begin{matrix}N(C_3H_5)\cdot CH<CH_3\\ NH\text{——}CH<NH\\ \qquad\qquad\quad CH_3\end{matrix}.$$

(*b.*) *Phenylthiocarbimide and Aldehyde-ammonia.**

Warm, concentrated alcoholic solutions of 1 mol. thiocarbimide and 2 mols. aldehyde ammonia were mixed. The mixture "set" instantly to a yellowish-white paste. This was freed from the mother-liquor, which it obstinately retains, by squeezing in a cloth. The mass was recrystallised three times from warm alcohol, and the product dried over sulphuric acid in a vacuum. The pure substance thus obtained crystallises in fine, silver-white needles, which melt at 148—149°, with browning and copious evolution of gas.

The substance is insoluble in water, but decomposed by boiling with it; soluble in alcohol, ether, and chloroform. The alcoholic solution is freely desulphurised by warming with alkaline lead solution. Silver nitrate in excess gives a white precipitate, which rapidly blackens, even in a freezing mixture.

Results of analysis:—

0·2020 gram, burnt with lead chromate, gave 0·4405 CO_2 and 0·1331 H_2O,

or C = 59·46 per cent.; H = 7·32 per cent.

0·2188 gram gave 0·4769 CO_2 and 0·1465 H_2O,

or C = 59·43 per cent.; H = 7·43 per cent.

0·2070 gram, burnt with copper oxide, gave 32·6 c.c. N, at 9° C. and 777 mm.,

or N = 19·36 per cent.

* See note under ethyl thiocarbimide, *ante*.

0·4600 gram evaporated to dryness with sodium hydrate solution and fused with nitre, gave 0·4943 gram $BaSO_4$,

or S = 14·77 per cent.,

from which the formula $C_{11}H_{15}N_3S$ is deduced.

		Theory.	Experiment.			
			I.	II.	III.	IV.
C_{11}	131·67	59·66	59·46	59·43	—	—
H_{15}	15·00	6·79	7·32	7·43	—	—
N_3	42·03	19·04	—	—	19·36	—
S	31·98	14·49	—	—	—	14·77

The structural formula (provisional) is—

$$SC\begin{matrix}<N(C_6H_5)\cdot CH<CH_3\\ <NH\ \ \ CH<CH_3\end{matrix}.$$

A homologue of the latter was next obtained.

(*c.*) *Phenylthiocarbimide and Valeraldehyde-ammonia.*

Alcoholic solutions were mixed; on warming, a precipitate separated, which was drained and pressed. The mass was twice recrystallised from alcohol. Fine snowy-white needles were thus obtained, which, when dried over sulphuric acid in a vacuum, melt with decomposition at 152—153°. The dry substance becomes so electrical on slight friction that the particles fly about.

The following data were obtained :—

0·2057 gram, burnt with lead chromate, gave 0·5036 CO_2 and 0·1780 H_2O,

or C = 66·76 per cent.; H = 9·61 per cent.

0·2043 gram, burnt with copper oxide, gave 23·4 c.c. N at 7° C. and 77 mm.,

or N = 14·07 per cent.

0·2988 gram treated with sodium hydrate and nitre (see above) gave 0·2330 $BaSO_4$,

or S = 10·72 per cent.,

which agrees with the formula $C_{17}H_{27}N_3S$.

			Theory.	Experiment.		
				I.	II.	III.
C_{17}	203·49	.....	66·83	66·76	—	—
H_{27}	27·00	.....	8·86	9·61	—	—
N_3	42·03	.....	13·80	—	14·07	—
S	31·98	.....	10·50	—	—	10·72

The structural formula may be written—

$$SC<\begin{matrix}N(C_6H_5)\cdot CH<\begin{matrix}C_4H_9\\NH\end{matrix}\\NH\text{——}CH<\begin{matrix}\\C_4H_9\end{matrix}\end{matrix}.$$

(d.) Orthotolylthiocarbimide and Aldehyde-ammonia.

These substances unite at once when warm alcoholic solutions are mixed, the contents of the vessel "setting" to a snow-white mass. The yield is large—over 90 per cent. of the theoretical, but as this substance, like all the preceding, is decomposed by hot alcohol, the final yield of pure substance is small. The crude compound was recrystallised three times from warm alcohol: thus were obtained short, white prisms, insoluble in water, and melting at 158—159° with decomposition and evolution of gas.

The substance, dried over sulphuric acid in a vacuum, gave the following results on analysis:—

0·2264 gram, burnt with lead chromate, gave 0·5075 CO_2 and 0·1548 H_2O,

or C = 61·13; H = 7·59.

0·2930 gram, burnt with copper oxide, gave 45·1 c.c. N, at 10° C. and 755 mm.,

or N = 18·30 per cent.

0·3250 gram, treated with sodium hydrate and nitre, gave 0·3236 $BaSO_4$.

or S = 13·68 per cent.,

from which the formula $C_{12}H_{17}N_3S$ is deduced.

			Theory.	Experiment.		
				I.	II.	III.
C_{12}	143·64	.....	61·21	61·13	—	—
H_{17}	17·00	.....	7·24	7·59	—	—
N_3	42·03	.....	17·91	—	18·30	—
S	31·98	.....	13·62	—	—	13·68

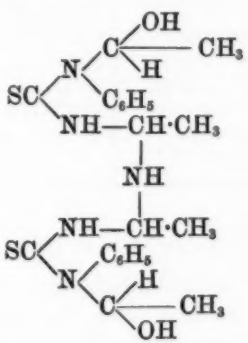
The reaction may be formulated as in the case of the isomeric benzyl compound, and the structure represented thus:—

$$SC\begin{cases} N(C_6H_4\cdot CH_3)\cdot CH\begin{cases} CH_3 \\ NH \end{cases} \\ N\text{———}CH\begin{cases} NH \\ CH_3 \end{cases} \end{cases}.$$

Reference has been made in the early part of this paper to the fact that R. Schiff (*Ber.*, **9**, 565) has also obtained compounds by the union of aldehyde-ammonia with certain "mustard oils." As his method of operating was essentially the same as that which I have described above, whilst on the other hand, the resulting compounds were quite different, I must indicate briefly the nature of his results.

(I.) $C_6H_5\cdot NCS + C_2H_4O,NH_3$.

By the action of these substances upon one another in alcoholic solution, Schiff obtained a compound to which he assigns the formula $C_{22}H_{31}N_5O_2S_2$. The structure he considers may be expressed by the following formula, which though not proved, "accords perfectly with the mode of formation and reactions."



The melting point of this substance is given at 148°; the compound which I obtained from the same materials melts at 148—149°.

For the purpose of comparison, I here tabulate the analytical results obtained by Schiff and by myself, together with the values calculated for the respective formulæ $C_{22}H_{31}N_5O_2S_2$ and $C_{11}H_{15}N_3S$.

	$C_{22}H_{31}N_5O_2S_2$ (Schiff).				$C_{11}H_{15}N_3S$ (Dixon).		
	Theory.	Experiment.			Theory.	Experiment.	
		I.	II.			I.	II.
C	57·22	57·53	57·26	C	59·66	59·46	59·43
H	6·73	7·05	6·95	H	6·79	7·32	7·43
N	15·21	15·30	—	N	19·04	19·36	—
S	13·89	14·42	—	S	14·49	14·77	—
O	6·95	—	—				

(II.) $C_3H_5{\cdot}NCS + C_2H_4O,NH_3$.

The compound obtained by the union of these compounds is described as having a similar constitution to the preceding. Empirical formula $C_{16}H_{31}N_5S_2O_2$; m. p. 107—108°. The compound similarly obtained by myself has the empirical formula $C_8H_{15}N_3S$; m. p. 108—109°.

I append, as before, a table of analytical results with corresponding calculated values.

	$C_{16}H_{31}N_5S_2O_2$ (Schiff).			$C_8H_{15}N_3S$ (Dixon).	
	Theory.	Experiment.		Theory.	Experiment.
C	49·30	49·30	C	51·82	51·87
H	7·98	8·12	H	8·11	8·75
N	18·03	—	N	22·75	23·13
S	16·46	—	S	17·30	17·58
O	8·23	—			

(III.) $C_2H_5{\cdot}NCS + C_2H_4O,NH_3$.

The compound of ethylthiocarbimide with aldehyde-ammonia obtained similarly to the two preceding compounds, is described as having an analogous composition, and to it a similar structure is assigned. The melting point is given as 118—119°. Empirical formula $C_{14}H_{31}N_5S_2O_2$. The compound obtained by me corresponds

with the description "white silvery needles" given by Schiff to the ethyl-compound; but its melting point is, as already stated, 135—136°, and its empirical formula $C_7H_{15}N_3S$.

As before, I give a table of comparative data.

	$C_{14}H_{31}N_5S_2O_2$ (Schiff).			$C_7H_{15}N_3S$ (Dixon).	
	Theory.	Experiment.		Theory.	Experiment.
C.....	45·97	46·30	C.....	48·49	48·64
H.....	8·50	8·50	H.....	8·68	8·77
N.....	19·21	—	N.....	24·32	24·94
S.....	17·54	—	S.....	18·50	18·16
O.....	8·78	—			

As I have directly determined all the constituents of each of the substances I obtained, and the analyses add up fairly satisfactorily, it is obviously impossible to admit that my compounds contain oxygen; yet their characters agree, in the main, with those described by Schiff. In his paper he states, that experiments directed with a view to determine whether hydroxyl-groups (whose existence he assumes) were present, led to no result. If the substances I obtained are really identical with Schiff's compounds, I can only conclude that he did not obtain them in a sufficiently pure state for analysis.

The structural formulæ given by myself are only provisional, but I hope shortly to be in a position to make a further communication, in which the constitution of these compounds shall be dealt with.

Chemical Laboratory,
University of Dublin,
March 1st, 1888.

XXXIV.—*A New Method of Estimating Nitrites, either alone or in presence of Nitrates and Chlorides.*

By T. Cuthbert Day.

In most text-books on chemistry a method is given for the preparation of nitrogen by heating a mixture of potassium nitrite and ammonium chloride, the change being represented by the equation—

$$NO_2K + NH_4Cl = KCl + 2OH_2 + N_2,$$

which may be simplified by saying that ammonium nitrite, when heated, splits up into nitrogen and water, thus:—$NO_2{\cdot}NH_4 = N_2 + OH_2$, the quantity of nitrogen produced being exactly double of that present as nitrous acid in the nitrite.

The method here given consists in applying this well-known reaction quantitatively. I have never seen any mention of the use of this reaction for quantitative purposes, and I scarcely think that a method, based on its use, would have been omitted in any work on analytical chemistry if accurate results had been obtained by its means.

In order to test the accuracy of the method I have devised, I prepared a quantity of pure silver nitrite, NO_2Ag, and determined the amount of nitrogen it contained, comparing the results obtained with that required by the known composition of the salt. The process is conducted in the following way:—

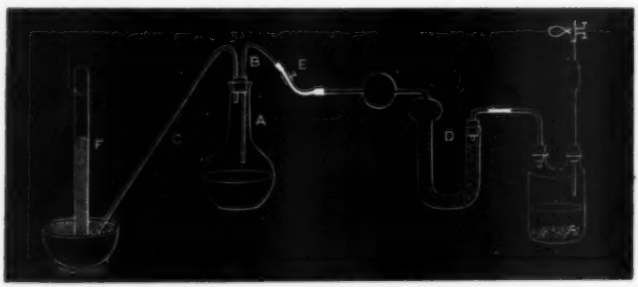


Fig. 1.

The solution containing the nitrite is introduced into the flask A (Fig. 1) (about 75 c.c. capacity), and an excess of solid ammonium chloride is then added till the solution is thoroughly saturated. It is important that the solution should be concentrated, otherwise considerable difficulty will be found in driving off the last traces of nitrogen. The flask is closed by a cork carrying the capillary tube B

and the delivery tube C of somewhat wider bore, 1·5 to 2·0 mm. Carbonic anhydride, generated from white marble and hydrochloric acid, in the apparatus shown in the figure, is then allowed to flow through the flask until all the air is removed. The small U-tube, D, is filled with glass beads moistened with a little weak potash solution, and is intended to intercept any acid spray which may be carried over by the current of gas.

As soon as it is considered that the whole of the air in the flask is displaced by carbonic anhydride, the screw-tap E is closed, and the flask disconnected from the carbonic anhydride apparatus. The end of the delivery tube C is now brought under the graduated absorption-tube F, which contains mercury and a few c.c. of strong potash solution to absorb the carbonic anhydride. The solution in the flask is now heated till it boils. As long as any nitrogen is given off the boiling liquid effervesces freely, but, as soon as the last traces have been expelled, the boiling assumes the peculiar bumping character noticed in water free from dissolved gas. The boiling is continued till all the nitrogen produced in the reaction has been carried over by the steam and collected in the absorption-tube. The screw-cock E may now be opened, while the liquid is still boiling, and the flask removed.

The absorption-tube containing the collected gas is removed to a vessel full of water, the mercury is allowed to fall out, and the volume of nitrogen obtained is measured after standing a few hours. The observed volume of nitrogen, when due allowance has been made for temperature, pressure, and tension of aqueous vapour, is *halved*, its weight calculated, and we have then all the data necessary for calculating the amount present in the nitrite under analysis.

The following experiments will show the degree of accuracy attainable by this method :—

The weighed quantity of silver nitrite was, in each case, dissolved in hot water and decomposed by a solution of sodium chloride. The solution was filtered through a small filter into the flask A, and the precipitated silver chloride washed repeatedly with small quantities of hot water, adding the washings to the solution in the flask :—

	Gram NO_2Ag.		Gram N. Half vol.	P. c. N.	P. c. N. NO_2Ag. Theory.	P. c.
Expt. 1.	0·1364	gave	0·012136	= 8·90	9·02	Loss 0·12
„ 2.	0·1700	„	0·015579	= 9·12	„	Gain 0·10
„ 3.	0·1712	„	0·015452	= 9·02	„	Exact.

I repeated the determinations in presence of excess of potassium nitrate. About 0·5 gram of this salt was added to the solution in each experiment :—

	Gram NO_3Ag.		Gram N. Half vol.	P. c. N.	P. c. N. NO_3Ag. Theory.	
Expt. 1.	0·1716	gave	0·015455	= 9·12	9·02	Gain 0·10
„ 2.	0·1808	„	0·016556	= 9·16	„	Gain 0·14

The results of these two experiments show that the presence of the nitrate does not affect the accuracy of the determinations.

XXXV.—*The Action of Acetone on Ammonium Salts of Fatty Acids in presence of Dehydrating Agents.*

By Dr. S. Ruhemann and D. J. Carnegie.

Some years ago, Zanoni (*Ber.*, **15**, 528) investigated the action of phosphoric anhydride on a mixture of acetamide and glycerol, and obtained β-picoline as a product of the reaction. Afterwards Hesekiel (*Ber.*, **18**, 911 and 3091) more thoroughly studied the reaction, and found that it involves the previous formation of acraldehyde, whilst the acetamide acts merely as a convenient source of ammonia, which, combining with the acraldehyde under the influence of the dehydrating agent, yields β-picoline in accordance with the following equation:—

$$2C_3H_4O + NH_3 = C_6H_7N + 2H_2O.$$

Hesekiel extended this reaction to the formation of the higher members of the pyridine series, using aldehydes instead of glycerol. Acetic aldehyde, for instance, he found to be first transformed by phosphoric anhydride into crotonic aldehyde, which in turn condensing with the ammonia derived from the acetamide, forms methylethylpyridine. This transformation of the aldehydes of the fatty series into the homologues of pyridine induced us to investigate analogous methods involving ketones instead of aldehydes.

Briefly stated, our experimental method consisted in heating mixtures of acetone and ammonium salts of fatty acids with dehydrating agents. In our first experiments, dehydration was effected by heating the mixture with zinc chloride in sealed tubes at a temperature of 250° for about four hours; but the pressure of the gases evolved under these conditions was so great as to cause much inconvenience. In our later experiments, phosphoric anhydride was substituted for zinc chloride, and the reaction was allowed to proceed in ordinary flasks fitted with reflux condensers. The charge for each flask was—

30 grams of acetone,
40 grams of ammonium salt,
35 grams of phosphoric anhydride.

After 24 hours' heating on the sand-bath, the contents of each flask were submitted to distillation in a current of steam in order to separate the hydrocarbons which are always formed in this reaction; excess of solid potash was then added to each flask, care being taken to keep the temperature low the while, and the resulting strongly alkaline liquid subjected to a second distillation with steam. The greater part of the base formed appeared as an oily layer floating on the surface of this second distillate. To liberate that portion of the base which is dissolved in the water of the distillate, solid potash was added thereto, since the base, though fairly soluble in water, is insoluble in concentrated potash solution. The base was finally dried over solid potash, and fractionally distilled through the temperature interval 80—200°.

The first fraction (80—160°) did not give a platinochloride. The second fraction (161—163°) on treatment with hydrochloric acid and platinic chloride gave a platinochloride, but at the same time an oil, undoubtedly a hydrocarbon, rose to the surface of the liquid. The platinochloride was purified in the usual way by repeated decomposition by hydrogen sulphide followed by repeated precipitation with platinic chloride. It was dried at 100°, and burnt in a stream of oxygen. As will be seen from the appended numbers the analysis undoubtedly proved it to have the composition $(C_9H_{15}N)_2,H_2PtCl_6$.

	Theory.	Found.
Pt	28·4	28·3
C.....	31·6	31·4
H	4·68	4·7
N	4·06	4·07

Each of the fractions (165—167°), (170—180°), (180—185°), gave platinum salts which were purified by recrystallisation from water. *In all cases, the analyses of these salts gave a mean of* 28·3 *per cent. of platinum;* hence it is clear that the chief product of the reaction of acetone on ammonium acetate in the presence of phosphoric anhydride is the base $C_9H_{15}N$; but that other bases of higher boiling point are also present in small quantity is evident from the behaviour of the liquid during distillation.

The mixture of hydrocarbons formed along with the base $C_9H_{15}N$ in this reaction was also examined, and was found to consist chiefly of mesitylene (b. p. 165—167°) mixed with small quantities of hydro-

carbons of higher boiling points. The analysis of the fraction 165—167° gave the following result:—

	Theory for mesitylene.	Found.
C	90·0	89·3
H	10·0	10·2

It should, in this connection, be noted that when zinc chloride is used to dehydrate, much more hydrocarbon and much less base is formed than when phosphoric anhydride is used.

Experiments similar to the foregoing were now made with ammonium formate and ammonium butyrate; and, from the analyses of the platinochlorides, we found that the bases formed in each case are identical with the base $C_9H_{15}N$ already prepared from ammonium acetate:—

	Analyses of Pt salt of base from $H{\cdot}COONH_4$.	Analysis of Pt salt of base from $C_3H_7{\cdot}COONH_4$.	Theory for $(C_9H_{15}N)_2,H_2PtCl_6$.
Pt	28·42	28·6	28·4

The mixture of hydrocarbons formed in the case of ammonium formate undoubtedly consisted largely of mesitylene as before. In the case of ammonium butyrate, the bye-product distilled over almost completely at 110—113°. As it could not possibly be mesitylene, an analysis was made. The appended numbers show that the substance was not, as we had anticipated, a hydrocarbon, but the ethyl salt of butyric acid:—

	Theory for $C_3H_7{\cdot}COOC_2H_5$.	Found.
C	62·0	61·68
H	10·3	10·28

The identity of the compound was further proved by the fact that the product of its hydrolysis gave the iodoform reaction. From these experiments, it follows that in all cases only the ammonia of the salts plays a part in the formation of the base $C_9H_{15}N$. This base is identical in all its properties with that isolated by Heintz (*Annalen*, **174**, 167, and **183**, 276) from the products of the reaction of ammonia and acetone, and which was called by him dehydrotriacetonamine.

Canzoneri and Spica (*Ber.*, **18**, 51 and 331) obtained it as chief product on heating a mixture of acetone and acetamide with zinc chloride at 135—140°. They also studied the action of reducing agents on the base, and found that it was thus transformed into methylated piperidines. From these observations, we may conclude that dehydrotriacetonamine is a hydrogenised pyridine-derivative. Accordingly, we now tried the action of mild oxidising agents on the

base $C_9H_{15}N$, in the hopes that we might by this means dehydrogenise it, and so obtain some well-defined member of the pyridine series. Some of the base (boiling at 161—163°) was treated with a filtered solution of bleaching powder; the mixture became warm, and a precipitation of calcium hydrate took place. After allowing it to remain for an hour, the mixture was heated for some time on the water-bath, and then distilled with steam. In this way we obtained an oil differing from the original base in its very pungent odour, and also in the fact that it was heavier than water. We had merely succeeded, however, in chlorinating the base, not in reducing it. The chlorine-derivative obtained was exceedingly unstable; on attempting to distil it, sudden decomposition took place at 80°, and chloroform distilled over in large quantity. An analysis of the unpurified substance was made, but no conclusions could be drawn from the result, viz., 27·7 per cent. Cl.

Again, in the hopes of obtaining a pyridine-derivative, we treated the chlorine-derivative with alcoholic potash, and then distilled in a current of steam. On saturating the distillate with potash, a fair quantity of a light oil was obtained. This was separated, dried over solid potash, and distilled. It distilled over almost completely between 78° and 79°. Three analyses and three vapour-density determinations were made, which showed that the action of alcoholic potash on the chlorine-derivative does not simply remove haloid acid, and give a pyridine-derivative as we had hoped, but that a more deep-seated decomposition takes place, resulting in the formation of large quantities of an isopropyl alcohol hydrate of the formula C_3H_8O,H_2O.

Appended are the results of analysis:—

	Theory for $C_3H_{10}O_2$.	Found. I.	II.	III.
C	46·15	46·48	46·36	45·91
H	12·82	12·6	12·67	13·7

Theoretical vapour-density of $C_3H_{10}O_2$, referred to hydrogen.	Found.
39	39·5

Hydrates of isopropyl alcohol have already been observed, but so far as we are aware the known hydrates do not include the one above referred to. Erlenmeyer (*Annalen*, **126**, 308) describes a hydrate of the formula $2C_3H_8O,H_2O$; whilst Linneman (*Annalen*, **136**, 40) has isolated hydrates having the compositions $3C_3H_8O,2H_2O$ and $3C_3H_8O,H_2O$.

University Laboratory, Cambridge.

XXXVI.—*Carboxyl-derivatives of Benzoquinone.*

By J. U. Nef.*

Chloro-, bromo-, hydroxy-, nitro-, and amido-derivatives of benzoquinone have long been known, but attempts to obtain carboxyl-derivatives have hitherto been unsuccessful.

The following experiments, undertaken with the intention of filling up this gap, were carried out at the suggestion of Prof. v. Baeyer, and it is an especial pleasure to the author to have this opportunity of expressing his gratitude to Prof. v. Baeyer for the kindness and interest shown him during his stay in Munich.

Durene was chosen as the starting-point for the experiments, on account of the especial interest attaching to the production of quinonetetracarboxylic acid, $C_{10}H_4O_{10} = C_6O_2(COOH)_4$, which has the same percentage composition as croconic acid, $C_5H_2O_5$, one of the products obtained by Gmelin (*Gmelin, Handbuch*, 4 Aufl., **5**, 478) from the explosive bye-product formerly obtained in the preparation of potassium.

The Russian chemist, Basaroff (*Dict. de Chemie par Würtz*, **2**, 1363), expressed the opinion that croconic acid and quinonetetracarboxylic acid were identical, but very recently Nietzki and Benckiser (*Ber.*, **19**, 293, 772), by a series of remarkable experiments, have shown that croconic acid has the formula $C_5H_2O_5$, thus rendering it impossible that it can be identical with a derivative of benzene. The following synthesis of ethylic quinonetetracarboxylate confirms the conclusion that the two compounds are totally different.

A close investigation of ethylic quinonetetracarboxylate has led to the discovery of a series of compounds which stand in a remarkably close relation to ethylic succinosuccinate and its derivatives. A study of durylic-acid-quinone, $C_6O_2(CH_3)_2{\cdot}COOH$, has shown that carboxylated quinones are very unstable substances, and that the carboxyl-group, which is usually so stable in benzene-derivatives, can easily be displaced by other groups; the nitro-group, for example. On the whole, however, they exhibit the general chemical reactions characterising other quinone-derivatives. On reduction, they take up two atoms of hydrogen, forming colourless quinols, which on oxidation yield the original quinone.

A very noteworthy fact is the existence of many carboxyl-paradihydroxy-derivatives of benzene, which cannot under any conditions be oxidised to the corresponding quinones. The oxidation to a

* Compare *Annalen*, **237**, 1.

quinone can only be accomplished in the case of hexa-substituted benzene-derivatives, which in this respect exhibit a much greater stability than other incompletely substituted derivatives of benzene.

The durene used was obtained from the chemical factory of Langfeld and Reuter, Bramow, near Rostock, and was made from monobromopseudocumene, $C_6H_2(CH_3)_3Br$ [1 : 2 : 4 : 5] (m. p. 71°), by Fittig's method. It was not pure, as the boiling point ranged from 185° to 220°, and contained, moreover, a liquid boiling at about 170°, and a solid compound melting at 100°, and boiling at 240°.

Durylic acid was prepared from pseudocumidine, $C_6H_2(CH_3)\cdot NH_2$ [1 : 2 : 4 : 5], by Sandmeyer's method of displacing the amido- by the cyanogen-group (Haller, *Ber.*, **18**, 93). Although the yield of duronitrile is poor (10—15 per cent.), and the preparation of the acid therefore wearisome, this is by far the best method of making durylic acid, and the product obtained is pure (m. p. 149°). As pseudocumidine is now much used in the colour industry in making azo-dyes, and, therefore, easily procurable, I have recently tried to better the yield of duronitrile by modifying Sandmeyer's method somewhat. Cuprous cyanide was used, the solution in potassic cyanide being kept boiling over a flame, while the diazo-pseudocumene solution was added. After extracting with ether, washing the ethereal solution with dilute sodic hydrate and sulphuric acid, and distilling off the ether, the nitrile was distilled over with steam. It was thus obtained pure, fusing at 57·5°. It can be saponified quantitatively by heating it with concentrated hydrochloric acid (1·18) in a sealed tube at 160—170°. The yield thus obtained was about 50 per cent., which is far better than that afforded by the usual method.

The course pursued in the investigation was the following:—The durene was converted by the usual methods into duroquinone, $C_6O_2(CH_3)_4$. As attempts to oxidise the methyl-groups to carboxyl-groups were unsuccessful, the durene was used solely to make durylic acid which on nitration gives dinitrodurylic acid; this acid was then converted into durylic-acid-quinone and pyromellithic-acid-quinone.

I. *Duroquinone from Durene.*

Dinitro-durene was made according to Jannasch and Fittig's method (*Zeit. f. Chem.*, 1870, 161). The durene (5 grams) was added slowly to pure fuming nitric acid (1·49), 40 c.c., kept at a temperature below 0°. The substance rotates rapidly, and then dissolves with a passing deep-brown coloration. After allowing the mixture to remain for two hours, it is poured on to ice, when the dinitro-durene separates out as a white flocculent precipitate. By crystallisation from alcohol, it can be separated from an oily bye-product,

and obtained in colourless prisms melting at 205°. It has all the properties ascribed to it by Jannasch and Fittig; it dissolves easily in benzene and ether, sparingly in hot, and very little in cold alcohol. It sublimes without decomposition in needles, and volatilises with steam. It is unusually stable in the presence of oxidising agents; dilute nitric acid, or a mixture of 1 vol. glacial acetic acid, 1 vol. concentrated nitric acid, and 1 vol. of water (in which the substance dissolves), not having the slightest action on it.

Dinitrodurol is best reduced as follows:—A hot solution of the substance in acetic acid is treated with zinc-dust until it no longer gives any turbidity on addition of water. The zinc is then precipitated from the diluted solution with sulphuretted hydrogen, and the filtrate concentrated. On addition of sodic hydrate, diamidodurene is precipitated in colourless pearly plates; this was not analysed, but converted directly into duroquinone. It is easily soluble in chloroform and alcohol; less so in ether. When exposed to the air in solution, or in a moist condition, it turns green. The hydrochloride of the base in sparingly soluble in concentrated hydrochloric acid. An aqueous solution thereof treated in the cold with ferric chloride, platinic chloride, or sodic nitrite is oxidised to duroquinone. In the case of platinic chloride, the addition of alcohol precipitates ammonium platinochloride, whilst duroquinone remains in solution, $C_6(CH_3)_4(NH_3Cl)_2 + H_2PtCl_6 + 2H_2O + O = C_6(CH_3)_4O_2 + (NH_4)_2PtCl_6 + 2HCl + H_2O$. A similar easy elimination of the amido-groups with formation of a quinone was also observed in the case of diamidodurylic acid.

The duroquinone was made by treating a solution of diamidodurene in hydrochloric acid with an excess of ferric chloride in the cold. A temporary deep-green coloration is noticed, and then the solution becomes yellow and the quinone crystallises out in yellow needles. The yield is almost quantitative and the product obtained is pure. If the diamidodurene is not isolated after the reduction with zinc-dust, and the ferric chloride is added directly to the acetic acid solution (from which the zinc has been removed), the quinone is obtained in small quantity as a very dark-coloured impure product.

Duroquinone was obtained by crystallisation from light petroleum in beautiful, long, yellow needles, melting at 111°.

0·1220 gram substance dried in a vacuum gave 0·3259 gram CO_2 and 0·0815 H_2O.

	Calculated for $C_6(CH_3)_4O_2$.	Found.
C	73·18	72·86
H	7·32	7·42

The quinone is volatile with steam, and sublimes at 100° in needles,

which possess a feeble but distinct odour characteristic of quinone. It is very easily soluble in alcohol, ether, chloroform, and in hot light petroleum; insoluble in water or alkalis. It was not possible under any condition to oxidise the methylated side-chains to carboxyl; oxidising agents in alkaline, neutral, or acid solution, decomposed the benzene ring completely. Worthy of note is the great stability of duroquinone in the presence of concentrated nitric acid (1·4), in which it dissolves with ease, but even after long heating on a water-bath remains in great part unchanged.

Treated with zinc-dust and acetic acid, the quinone is reduced, and on adding water, a colourless substance melting at about 210° is precipitated. Oxidising agents, such as ferric chloride or nitric acid, oxidise it again to duroquinone. It is probable that the substance is dihydroxydurene, but want of material has prevented me from obtaining the product in amount sufficient for an analysis.

II. *Dinitrodurylic Acid out of Durol.*

Durylic Acid, $C_6H_2(CH_3)_3 \cdot COOH$.—Jannasch (*Zeit. f. Chem.*, 1870, 449, and 1871, 33) has shown that durene heated for a long time with dilute nitric acid, yields, in about equal amount, two acids, one of which, durylic acid, $C_6H_2(CH_3)_3 \cdot COOH$, is volatile with steam; the other, cumidic acid,* $C_6H_2(CH_3)_2(COOH)_2$, is not volatile with steam. In my experiments, however, the great object was to obtain as much of the durylic acid as possible. When durene is heated with dilute nitric acid for three or four hours only, and the acid formed is then separated from unchanged durene, I find that durylic acid alone is formed. Durylic acid is also the sole oxidation-product obtained on treating a solution of durene in acetic acid with the calculated amount of chromic acid also dissolved in acetic acid. The yield in this case is, however, not so good as when the following method is employed.

20 grams durene is heated for three to four hours, with 500 c.c. dilute nitric acid (1 vol. concentrated nitric acid, sp. gr. 1·4, to 3 vols. water), taking care to add a few pieces of porous porcelain to prevent bumping. After filtering from the nitric acid, the product is treated with dilute sodium carbonate solution and the unchanged durene heated again with nitric acid as above. After the second and third treatment with sodium carbonate an insoluble yellowish oil remains which can easily be separated from the soda solution by means of ether. On distilling off the ether, an oil is left which contains nitrogen and undergoes little change on further heating with nitric acid.†

* This has recently been shown to consist of two isomeric acids (Schnapauff, *Ber.*, **19**, 2510).

† The oil has a peculiar camphor-like odour, and is very easily soluble in ether.

On adding hydrochloric acid to the mixed sodium carbonate solution, impure durylic acid separates as a flocculent precipitate. It is first treated in acetic acid solution with zinc-dust, to get rid of the nitro-products possibly formed, and then distilled with steam. As the whole is volatile with steam, there can be no bibasic cumidic acid formed. The durylic acid thus driven over with steam is pure, melting at 149°, and has all the properties assigned to it by Jannasch (*Zeit. f. Chem.*, 1870, 449).

It is very sparingly soluble even in boiling water and volatilises with steam without melting. The yield obtained by the above method was 15—20 grams of impure durylic acid and 20—22 grams of oily bye-product from 40 grams of durene. In the further experiments, the impure durylic acid, obtained on adding hydrochloic acid to the soda solutions, was used.

(2.) *Dinitrodurylic Acid*, $C_6(NO_2)_2(CH_3)_3 \cdot COOH$.—The nitration of durylic acid, according to Gissmann's method, was not found advantageous, as the reaction is too violent. The following process gives a quantitative yield:—20 grams finely pulverised durylic acid (dried at 100°) is dissolved in pure concentrated sulphuric acid, and the solution cooled down to −10° or −15° by means of a freezing mixture. A solution of 28 grams potassic nitrate in concentrated sulphuric acid is now added as quickly as possible—taking care to stir well, and to keep the temperature below 5°.

A deep brown colour appears at first which changes finally to light yellow, while dinitrodurylic acid partly separates. After allowing the mixture to remain at the ordinary temperature for four or five hours, or over night, the solution is poured carefully on to ice. The nitro-acid separates out as a flocculent, yellowish precipitate which is collected and well washed. If pure durylic acid is used, the product thus obtained is sufficiently pure; if, however, the impure acid is employed, the nitro-derivative must be purified by means of its calcium salt. (Gissmann, *Annalen*, **216**, 208.)

The crude product is heated with water and finely pulverised marble until the reaction is neutral; on filtering and concentrating, the calcium salt crystallises out in colourless, radiating needles. When heated on platinum-foil, it explodes violently.

An analysis of the oil, as well as of a solid product obtained therefrom by cooling below 0° and pressing between filter-paper (melting point 35—40°), gave figures agreeing with those required by mononitrodurene. The oil, however, does not yield dinitrodurene on treatment with fuming nitric acid, and it is therefore more probable that the oil is a nitrate of a trimethylated benzyl alcohol. This is the more probable as, by oxidation with potassium permanganate in soda solution, acids are obtained which contain no nitrogen. In this way I succeeded in isolating an acid possessing all the properties of pyromellitic acid, and the analysis of the silver salt gave figures which are exactly those required by $C_6H_2(COOAg)_4$.

0·3155 gram substance dried at 180° gave 0·0760 gram $CaSO_4$ = 7·10 per cent. calcium; calculated, 7·32 per cent.

The free acid, obtained by the addition of hydrochloric acid to the purified calcium salt, is a yellowish, amorphous powder melting at about 205°. It has all the properties mentioned by Gissmann (*loc. cit.*).

The potassium salt is sparingly soluble in cold water, and crystallises in colourless, lustrous needles.

III. *Durylic Acid Quinone from Dinitrodurylic Acid.*

(1.) *Diamidodurylic Acid*, $C_6(NH_2)_2(CH_3)_3{\cdot}COOH$.—A solution of dinitrodurylic acid in acetic acid (50 per cent.) is treated with zinc-dust in small portions; a violent reaction takes place at first, and finally the solution becomes colourless. After filtering hot from the excess of zinc-dust, the solution is diluted with about 4 volumes of water and allowed to cool, when the diamidodurylic acid crystallises out almost completely in colourless, silky needles. The small portion remaining in solution is recovered by precipitating the zinc, concentrating the ammoniacal solution, and adding dilute acetic acid. The yield is almost quantitative.

For analysis, the substance was crystallised from water several times, and then dried carefully at 110°.

0·1642 gram anhydrous substance gave 0·1105 gram H_2O and 0·371 gram CO_2.

0·0950 gram anhydrous substance gave 12 c.c. nitrogen at 15° and 723 mm.

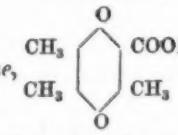
	Calculated for $C_{10}H_{14}N_2O_2$.	Found.
C	61·85	61·62
H	7·22	7·48
N	14·42	14·10

The figures obtained for carbon were at first always about 1 per cent. too low, because the substance sticks together on heating, and it is difficult to remove the last trace of water of crystallisation.

Diamidodurylic acid forms salts with bases and with mineral acids. The compounds with hydrochloric acid and with sulphuric acid are easily soluble in water. On adding platinic chloride to a solution of the hydrochloride in the cold, ammonium platinochloride separates and durylic-acid-quinone is formed. The oxidation to the quinone also takes place with equal ease on treatment with ferric chloride or sodic nitrite.

Diamidodurylic acid is sparingly soluble in cold alcohol or water; much more soluble in hot; it is insoluble in ether. It melts at 221°

with decomposition. When heated with acetic anhydride for several hours at 140°, an acetyl-derivative was formed. After getting rid of the acetic anhydride, the substance was dissolved in ammonia, and precipitated therefrom by hydrochloric acid; in this way, it was precipitated in colourless quadratic plates melting at about 275°. When heated in a test-tube, the substance loses carbonic anhydride, and a compound sublimes in colourless needles; it is insoluble in alkalis.

(2.) *Durylic-acid-quinone*,  .—This compound, the first carboxylated quinone-derivative known, is formed quantitatively on adding an excess of ferric chloride to a solution of pure diamidodurylic acid in hydrochloric acid, and allowing the mixture to remain for about half an hour. No colour reactions are noticed, but the yellow solution has a faint but distinct quinone-like odour. If the solution is sufficiently concentrated, part of the acid crystallises out in yellow rhombohedrons. The solution is extracted three or four times with ether, and the ether dried with calcium chloride; after distilling off part of the ether and allowing the remainder to evaporate spontaneously, the quinone acid remains as a dark-yellow, crystalline substance having a distinct quinone odour.

If the above directions are carefully followed, it is only necessary to wash away the traces of adhering ferric chloride with a little water in order to obtain a perfectly pure product. On heating with ferric chloride, or on trying to convert dinitrodurylic acid directly into the quinone without isolating the diamido-compound, a very impure yellow, oily product is obtained.

The crystals obtained from the ethereal solution are radiating flat needles of a deep yellow colour. Heated in a capillary tube, they become red at 127—129°, and decompose at 130° with brisk evolution of gas.

I. 0·1340 gram substance dried in a vacuum gave 0·3038 gram CO_2 and 0·065 gram H_2O.

II. 0·1540 gram substance dried in a vacuum gave 0·346 gram CO_2 and 0·076 gram H_2O.

	Calculated for $C_6O_2(CH_3)_3 \cdot COOH$.	Found. I.	Found. II.
C	61·85	61·83	61·68
H	5·15	5·40	5·52

Durylic-acid-quinone dissolves easily in alcohol and in other organic solvents, except light petroleum. It is sparingly soluble in cold

water, more soluble in hot water (the quinone odour is then especially noticeable), but does not crystallise out well on cooling. It dissolves in benzene in the cold unchanged, but, on heating, the yellow solution changes to an intense dark red. Durylic-acid-quinone differs from other quinones in being non-volatile and easily decomposed. Being an acid it decomposes soluble carbonates in the cold, and dissolves in alkalis and in ammonia with a deep yellow colour. The alkaline solutions can be partly evaporated without change. In other respects, the quinone acid resembles the other paraquinone compounds of benzene; thus, for example, it can be reduced in alkaline or acid solution to the corresponding quinol or paradihydroxy-compound which on oxidation yields the original quinone compound again.

An intermediate compound corresponding to quinhydrone was not noticed. Like quinone itself, the above quinone acid reacts with phenol and resorcinol, forming dark-red compounds.

On allowing a dilute alcoholic solution of the quinone acid to stand for two days with an excess of hydroxylamine hydrochloride, a yellow unstable compound containing nitrogen is formed; this is probably the quinoneoxime.

Of the salts of durylic-acid-quinone, the silver salt was prepared by adding silver nitrate to a concentrated solution of the neutral ammonium salt. It was thus obtained in yellow needles, little soluble in cold water, more so in hot. It is unstable towards heat and light, and explodes when heated quickly on platinum foil.

0·146 gram substance dried in a vacuum gave 0·041 gram H_2O, 0·2125 gram CO_2, and 0·0525 gram Ag.

	Calculated for $C_6O_2(CH_3)_3\cdot COOAg$.	Found.
C.....	39·87	39·70
H	2·99	3·12
Ag	35·88	35·96

A concentrated solution of the ammonium salt of durylic-acid-quinone treated with *lead acetate* gives the lead salt as an insoluble yellow amorphous precipitate. *Baric chloride* gives the barium salt as a yellow crystalline precipitate, dissolving on heating. *Copper sulphate* gives the copper salt as a pale-yellow, sparingly soluble granular precipitate.

(3.) *Dihydroxydurylic Acid*, $C_6(OH)_2(CH_3)_3\cdot COOH$.—Durylic-acid-quinone can be reduced quantitatively in alkaline or acid solution to dihydroxydurylic acid. In my first experiments, I used zinc-dust and sodic hydrate. A dilute solution of the substance in sodic hydrate was treated in the cold with zinc-dust added in small portions at a

time. The solution turns green, then violet, and finally becomes colourless; it is then acidified with concentrated hydrochloric acid, and extracted with ether. On distilling off the ether, a white amorphous mass remains, having a characteristic sweet smell. This method of reduction is uncertain on account of the instability of dihydroxydurylic acid in alkaline solution, and it is much better to reduce with sulphurous acid, which at once gives a pure product. On adding a concentrated cold aqueous solution of sulphurous acid to finely pulverised durylic-acid-quinone and shaking, the whole mass is converted into dihydroxydurylic acid without dissolving; in order to obtain a colourless product, the mixture is heated in a sealed tube at 100° for two to three hours, and then repeatedly crystallised out of water containing sulphurous acid. Dihydroxydurylic acid is thus obtained in colourless spheres, made up of very fine radiating needles; it melts at 210° with decomposition.

I. 0·1432 gram substance dried at 110° gave 0·3208 gram CO_2 and 0·084 gram H_2O.

II. 0·1556 gram substance dried at 110° gave 0·3485 gram CO_2 and 0·089 gram H_2O.

	Calculated for $C_6(OH)_2(CH_3)_3 \cdot COOH$.	Found. I.	Found. II.
C.....	61·27	61·10	61·08
H	6·13	6·52	6·36

This quinol dissolves easily in alcohol and ether, sparingly in benzene and chloroform. Ferric chloride added to a dilute alcoholic solution oxidises it, with passing green coloration, to the quinone. The colourless alkaline solution of the acid is unstable when exposed to the air, changing quickly to a yellow, red, red-violet, and finally to a deep violet. An ammoniacal solution of the acid reduces silver nitrate in the cold. Lead acetate, added to a solution of the ammonium salt, gives a colourless amorphous precipitate.

(4.) *Ethyl quinonedurylate*, $C_6O_2(CH_4)_3 \cdot COOC_2H_5$, was made by allowing the silver salt of durylic-acid-quinone to stand for 24 hours with a dry ethereal solution of ethyl iodide. The ethereal solution, filtered from the silver iodide, was washed with sodic carbonate, and dried by means of calcic chloride. After distilling off the ether, a yellow oil remained, which, on rubbing with a glass rod, solidified readily to yellow radiating needles. On recrystallisation from hot light petroleum, it was obtained in long yellow needles melting at 51°.

0·1225 gram substance dried in a vacuum gave 0·0706 gram H_2O and 0·2902 gram CO_2.

	Calculated for $C_6O_2(CH_3)_3 \cdot COOC_2H_5$.	Found.
C.....	64·86	64·61
H	6·31	6·40

The ethereal salt, unlike the free acid, is odourless. Like other quinones, it sublimes with ease, and without decomposition. It is easily soluble in alcohol and ether; insoluble in water or alkalis. It is saponified when heated with sodic hydrate.

(5.) *Ethyl Dihydroxydurylate*, $C_6(OH)_2(CH_3)_3 \cdot COOC_2H_5$.—On heating ethyl quinonedurylate with a concentrated aqueous solution of sulphurous acid it is reduced, and on cooling ethyl dihydroxydurylate crystallises out in needles. The substance may be purified by dissolving it in alcohol and adding water containing sulphurous acid to the hot alcoholic solution. It is thus obtained in colourless, broad needles melting at 109°, and having a characteristic sweet smell.

0·0935 gram substance dried in a vacuum gave 0·2185 gram CO_2 and 0·06 gram H_2O.

	Calculated for $C_6(OH)_2(CH_3)_3 \cdot COOC_2H_5$.	Found.
C.....	64·29	63·73
H	7·14	7·13

The ethereal salt is soluble in alcohol and other organic solvents except light petroleum. It is somewhat soluble in cold water; much more so in hot. It dissolves in sodic hydrate, forming a colourless solution; on heating, however, hydrolysis occurs and the colour of the solution changes to deep violet.

In alcoholic solution, ferric chloride oxidises it to the quinone with passing green coloration. Nitric acid (sp. gr. 1·4) also oxidises it to the quinone. An intermediate product corresponding to quinhydrone was not noticed.

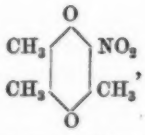
(6.) *Action of Concentrated Nitric Acid on Durylic-acid-quinone.*—Durylic-acid-quinone dissolves without change in nitric acid (sp. gr. 1·4) in the cold. On heating on a water-bath, however, a strong evolution of gas is observed. The addition of water now precipitates a beautiful, yellow, crystalline substance which is insoluble in alkalis, and therefore no longer an acid. Further investigation has shown that the carboxyl-group of durylic-acid-quinone has been displaced, and, in fact, quantitatively, by a nitro-group, according to the reaction:—

$$C_6O_2(CH_3)_3 \cdot COOH + HNO_3 = C_6O_2(CH_3)_3 \cdot NO_2 + H_2O + CO_2.$$

The resulting compound, nitropseudocumoquinone, is one of the most stable of quinone compounds.

By heating durylic-acid-quinone with alcoholic ammonia in a sealed tube at 100°, the elements of carbon dioxide are removed, and a deep-red solution is obtained. Want of material has prevented me thus far from investigating the product more closely.

These observations are in harmony with those of Hermann (*Annalen*, **211**, 343) in the case of paradihydroxyterephthalic acid. The latter when treated with concentrated nitric acid gives no terephthalic-acid-quinone, but 2 mols. CO_2 are eliminated in the cold with formation of nitranilic acid. All these facts go to show that the carboxyl-group in carboxylated quinone-compounds is very loosely bound.

Nitropseudocumoquinone,  , is formed quantitatively on heating durylic-acid-quinone on a water-bath for about half an hour with nitric acid (sp. gr. 1·4) until the evolution of carbonic anhydride ceases. On adding water, the quinone separates out completely and crystallises in yellow plates melting at 113°.

0·1485 gram substance dried in a vacuum gave 0·3023 gram CO_2 and 0·0655 gram H_2O.

0·230 gram substance dried in a vacuum gave 15 c.c. nitrogen at 16° and 710 mm.

	Calculated for $C_6O_2(CH_3)_3 \cdot NO_2$.	Found.
C.....	55·38	55·52
H.....	4·62	4·9
N.....	7·18	7·09

This substance is very stable. It sublimes easily and without decomposition. Heated on a water-bath for hours with concentrated nitric acid, it remains in great part unchanged. On crystallisation from nitric acid, light petroleum, or especially from dilute alcohol, it is obtained in yellow plates, melting at 113°, and possessing a faint but distinct quinone-like odour.

(7.) *Nitropseudocumoquinol*, $C_6(OH)_2(CH_3)_3 \cdot NO_2$.—This was obtained by treating nitropseudocumoquinone in a sealed tube at 100° with a concentrated solution of sulphurous acid in 25 per cent. alcohol. On cooling, the tube is filled with long, broad, yellow needles, which are quite pure, and remain unchanged on repeated treatment with sulphurous acid solutions. For analysis, the substance was crystallised from ether, when it was obtained in flat, yellow needles, melting at 106°.

0·1797 gram substance dried in a vacuum gave 0·3592 gram CO_2, and 0·0902 gram H_2O.

	Calculated for $C_6(OH)_2(CH_3)_3 \cdot NO_2$.	Found.
C.....	54·82	54·52
H	5·58	5·58

Nitropseudocumoquinol is easily soluble in chloroform, ether, and alcohol. It is somewhat soluble in hot water, crystallising therefrom in flat needles. Sodic hydrate colours it bluish-violet, and it then dissolves with a pale greenish-yellow colour. Ferric chloride or concentrated nitric acid oxidises it to the corresponding quinone.

On treating a solution of the quinone or of the quinol in acetic acid with zinc-dust, reduction takes place, and finally a colourless solution is obtained, which on exposure to the air soon becomes deep red-violet. On neutralising with sodic carbonate, after precipitation of the zinc as zinc sulphide, ether extracts a deep red substance, which with hydrochloric acid forms a colourless hydrochloride, crystallising in needles, and sparingly soluble.

IV. *Conversion of Dinitrodurylic Acid into Ethyl Quinonetetracarboxylate.*

(1.) *Dinitropyromellitic Acid*, $C_6(NO_2)_2(COOH)_4$*.—The oxidation of the three methyl side-chains in dinitrodurylic acid to carboxyl was carried out by means of potassium permanganate, and gave an almost quantitative yield.

20 grams of dinitrodurylic acid (dried at 100°) and 50 grams of anhydrous potassic carbonate were dissolved in 2 litres of water, and heated on a water-bath. To this, a solution of 72 grams of potassic permanganate was slowly added. At first oxidation takes place rapidly, but towards the end very slowly, and is finished after four or five days. The manganese dioxide formed was filtered off, and the filtrate concentrated. After acidifying with concentrated hydrochloric acid and dilute sulphuric acid, the solution was extracted four times with ether; on distilling off the ether, a white mass remained behind, consisting of a mixture of the tribasic and the tetrabasic acid. After many trials, the following method of separation was found to be exceedingly sharp. The mixture was dissolved in water and heated

* The direct nitration of pyromellitic acid seems to be impossible. This acid can be heated with a mixture of concentrated sulphuric acid and potassic nitrate for 10 hours in a sealed tube at 150° without the slightest change. The application of Burkhardt's method, by which, as is well known, terephthalic acid has been nitrated (*Berichte*, 10, 145) was, in this case, entirely fruitless.

on a water-bath with finely pulverised marble until the reaction was neutral, and alcohol (about 2 volumes) was then added to the concentrated filtrate, until no further precipitation took place. In this way the calcium salt of the tetrabasic acid is precipitated completely in pale-yellow needles, while the calcium salt of the tribasic acid remains in solution, and in fact cannot be precipitated at all by addition of more alcohol. The tribasic acid was then converted into the tetrabasic acid by renewed treatment with potassic permanganate. The last methyl-group in the tribasic acid is attacked by oxidising agents with great difficulty, so that it takes from four to five days to oxidise 10 grams. The yield was excellent; 20 grams of dinitrodurylic acid gave from 20 to 23 grams of pure anhydrous dinitropyromellittic acid.

The abovementioned calcium salt of dinitropyromellitic acid was purified by dissolving it in water and precipitating by addition of alcohol. It crystallises in pale-yellow needles. When heated in an air-bath at 180°, it loses its water of crystallisation, and becomes deep golden-yellow.

I. 0·1260 gram salt dried at 180° gave 0·0802 gram $CaSO_4$.
II. 0·1602 „ „ „ 0·1022 „ „

	Calculated for $C_6(NO_2)_2(COO)_4Ca_2$.	Found. I.	Found. II.
Ca.....	19·05	18·73	18·76

To obtain the acid, the purified calcium salt was dissolved in water, and the strongly acidified solution extracted three or four times with pure ether. On distilling off the ether and drying at 100°, pure dinitropyromellitic acid is left. The acid is colourless, has a very strong acid smell, and decomposes marble in the cold with violent evolution of carbonic anhydride. It crystallises from ether or water in long, silky needles. It is easily soluble in cold water, still more so in hot water, and deliquesces in ether vapour. It is also readily soluble in alcohol and acetic acid, but insoluble in chloroform, benzene, and light petroleum.

With the exception of the silver, lead, and barium salts, the salts of this acid are easily soluble in water, and most of them are precipitated from their aqueous solutions by alcohol. The barium salt is easily soluble in hot water, much less so in cold water. A separation of the tribasic and tetrabasic acids can also be accomplished by means of their barium salts, as the salt of the tribasic acid is much more easily soluble.

When heated in a capillary tube, dinitropyromellitic acid loses water (100—160°) and becomes slightly yellow. Above 160°, it

becomes gradually deeper and deeper yellow, and decomposes with violent evolution of gas, between 208° and 225°, according as the temperature rises slowly or quickly. If heated in an air-bath at 140° for several hours, the acid decomposes, and is converted into a deep-yellow substance.

When dried at 100°, the acid is colourless and anhydrous, as was deduced from the precipitation and analysis of the silver salt.

I. 10·2 grams acid gave 22·5 grams silver salt.
Calculated: 22·88 ,, ,,
II. 21·3 grams acid gave 47·6 ,, ,,
Calculated: 47·77 ,, ,,

The silver salt was prepared by adding a neutral solution of the ammonium salt of the acid to a hot solution of silver nitrate. It forms a stable, amorphous, yellow precipitate, quite insoluble in water. For analysis, it was dried at 100°, and as it explodes on heating, it was carefully mixed with the copper oxide.

I. 0·3954 gram substance gave 0·2278 gram CO_2 and 0·0210 H_2O.
II. 0·4115 gram substance gave 0·2340 gram CO_2 and 0·0120 H_2O.
0·223 gram substance gave 0·1650 gram AgCl or 0·1242 Ag.
0·5668 gram substance gave 18·75 c.c. nitrogen at 7° and 714 mm.

	Calculated for $C_6(NO_2)_2(COOAg)_4$	Found. I.	Found. II.
C	15·55	15·71	15·51
H	—	0·59	0·32
Ag.....	55·96	55·70	—
N	3·63	3·73	—

It is not possible to convert dinitropyromellitic acid into the normal ethereal salt by the ordinary methods. An alcoholic solution saturated with gaseous hydrogen chloride and allowed to stand for two days did not yield it, and the acid heated with alcohol and a few drops of concentrated sulphuric acid for two days on a water-bath remained in great part unchanged.

With reducing agents, the acid shows a very characteristic reaction; all reducing agents whether applied in neutral, acid, or alkaline solution produce a deep red coloration. Ether extracts from acid solutions a red substance; the deep red ethereal solution has a very marked yellowish-red fluorescence. The red substance remains unchanged even when heated with reducing agents for a long time; it is undoubtedly, as will be seen below from results obtained with the ethereal salt, free diamidopyromellitic acid. The reduction takes a

different course when granulated zinc and dilute sulphuric acid are used in the cold. In this case, a yellow solution is produced, from which ether extracts a yellow substance. The yellow ethereal solution has a marked green fluorescence.

The tribasic acid, methylparadinitrotrimellitic acid,

$$C_6(NO_2)_2(CH_3)(COOH)_3,$$

which is obtained along with dinitropyromellitic acid on oxidising dinitrodurylic acid, forms a deliquescent calcium salt. With basic lead acetate, it gives a fine yellow basic lead salt. The silver salt comes down after long heating with silver nitrate in sparingly soluble yellow plates.

The acid itself is easily soluble in hot water; much less so in cold. It dissolves with the greatest ease in alcohol and ether. It is obtained in long, colourless needles by crystallisation from water containing hydrochloric acid.

(2.) *Ethyl Dinitropyromellitate*, $C_6(NO_2)_2(COOC_2H_5)_4$.—The ethyl salt of dinitropyromellitic acid was prepared in considerable quantity by treating the silver salt with ethyl iodide. The neutral silver salt can be precipitated quantitatively as follows:—A solution of 20 grams of dinitropyromellitic acid, carefully neutralised with ammonium hydrate, is added slowly to a warm (50°) solution of 50 grams of silver nitrate. The silver salt was dried at 100°, and then allowed to stand over night with ethyl iodide ($1\frac{1}{2}$ times the calculated amount) and dry ether; to complete the reaction, the mixture was heated for five or six hours on a water-bath. The ethereal solution was now filtered from the silver iodide, washed with dilute sodic carbonate, and then dried with calcic chloride; after distilling off the ether, the solid ethyl salt was left sufficiently pure for farther work. For analysis, it was crystallised twice from alcohol, when it formed long, colourless needles melting at 130°.

0·1155 gram substance gave 0·2006 gram CO_2 and 0·0465 gram H_2O.

	Calculated for $C_6(NO_2)_2(COOC_2H_5)_4$.	Found.
C.....	47·37	47·38
H.....	4·39	4·47

It is easily soluble in benzene, chloroform, acetic acid, and acetone; less so in ether. By crystallisation from hot alcohol or light petroleum, it is obtained in beautiful needles. It dissolves in alcoholic ammonia with a fugitive red colour. The yield was seldom over 60 per cent. of the theoretical.

(3.) *Ethyl Diamidopyromellitate*, $C_6(NH_2)_2(COOC_2H_5)_4$.—Ethyl di-

nitropyromellitate, on reduction with zinc-dust and acetic acid, gives a beautiful red compound, which I long regarded as ethyl azopyromellitate. It was found impossible, in spite of repeated efforts, to reduce this substance further with elimination of the nitrogen. I thought therefore that it might possibly be an inner azo-compound, as it sublimes without decomposition like a quinone. I tried to ascertain its molecular weight by means of a vapour-density determination, using Victor Meyer's method, but without success.

Nevertheless the analytical figures obtained did not agree sharply; the hydrogen especially was always too high. Later, when I had larger quantities of the substance in my hands, and analysed a product purified with especial care, I obtained figures agreeing exactly with those required by ethyl diamidopyromellitate. Finally the formation and isolation of a colourless diacetyl-derivative by treating it with acetic anhydride, is a convincing proof that the red substance is actually a diamido-compound.

The deep red colour of the diamido-compound is now no longer remarkable, as v. Baeyer (*Ber.*, **19**, 430) has recently shown that ethyl paradiamidoterephthalate has the colour of potassic dichromate.

For reducing ethyl dinitropyromellitate, the following method was found most advantageous, and gave an almost quantitative yield. The substance was first dissolved in acetic acid, and to the hot solution a little water, and then zinc-dust in small portions at a time were added. When the addition of more zinc-dust no longer produced a violent reaction, and the red colour had changed to yellow, the solution was filtered hot from the zinc-dust, and poured slowly (stirring well) into a dish containing water. The diamido-compound then separated completely in yellow flakes, which soon changed to a red crystalline precipitate. For purification, the substance was dissolved in ether, washed with dilute sodic carbonate, and the ethereal solution, dried with calcic chloride, was then allowed to evaporate over sulphuric acid; the diamido-compound crystallised out in beautiful deep red four-sided prisms.

For analysis, the large crystals were mechanically picked out and dried at 100°. They melted at 134°, and sublimed without decomposition and without leaving any residue. When melted and allowed to solidify again, the substance has exactly the appearance of sealing-wax.

I. 0·1231 gram substance gave 0·2447 gram CO_2 and 0·0675 gram H_2O.

II. 0·1774 gram substance gave 0·3554 gram CO_2 and 0·1044 gram H_2O.

III. 0·1842 gram substance gave 0·3681 gram CO_2 and 0·1036 gram H_2O.

0·2970 gram substance gave 20·3 c.c. nitrogen at 19° and 723 mm.

	Theory for $C_6(NH_2)_2(COOC_2H_5)_4$.	Found. I.	II.	III.
C	54·55	54·20	54·64	54·50
H	6·06	6·09	6·54	6·25
N	7·07	7·47	—	—

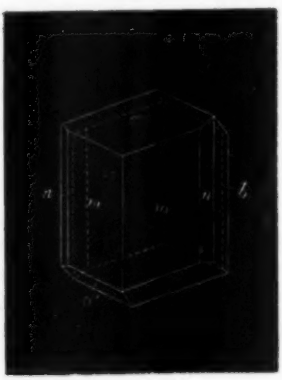
Ethyl Diamidopyromellitate.

Dr. W. Muthmann examined the above crystals of ethyl diamidopyromellithate in the mineralogical laboratory of P. Groth in Munich, and reports as follows:—

Monoclinic system: β 61° 17′.

$$a : b : c = 0{\cdot}66964 : 1 : 0{\cdot}62686.$$

Planes: $m = (110) = \infty P$.
$c = (001) = 0P$; $0 = (\bar{1}11) = +P$.
$b = (010) = \infty\breve{P}\infty$; $n = (110) = \infty\breve{P}2$.



The majority of the crystals showed only the crystal faces m, c, and b.

	Found.		Calculated.	
$(110) : (1\bar{1}0) =$	*60°	50′	—	—
$(110) : (001) =$	*65	31	—	—
$(010) : (\bar{1}11) =$	*60	55	—	—
$(\bar{1}10) : (\bar{1}11) =$	53	39	53°	35′
$(110) : (120) =$	19	7	19	10
$(010) : (001) =$	90	3	90	—

Colour: reddish-orange (Radde's International colour scale). The plane of the optic axes is parallel to the plane of symmetry.

One bisectrix lies in the acute angle of the crystallographic axes and forms with the vertical one an angle of $15\frac{1}{2}°$. An optical axis comes out very nearly perpendicular to (001). From these data, the axial angle is found to be approximately 85—90°.

The crystals are very soft, and possess a remarkably perfect cleavage in the direction (001).

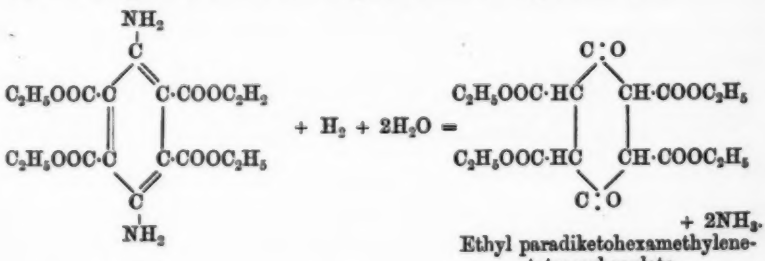
Ethyl diamidopyromellitate has feeble basic properties. On adding to it concentrated hydrochloric acid, it becomes colourless; and on diluting with an equal volume of water and heating, the colourless salt dissolves, and crystallises out again in needles on cooling. More water decomposes the salt, and the free base separates out in beautiful rhombic plates. The diamido-compound dissolves in concentrated sulphuric acid with a pale-yellow colour; water precipitates the free base again unchanged.

The substance dissolves easily in alcohol, ether, and acetic acid. The ethereal solution is red, and shows a very marked yellowish-red fluorescence. On saponification with alcoholic potash, and acidifying, ether extracts from the solution a red substance identical with that obtained by the reduction of dinitropyromellitic acid.

On treating a hot alcoholic solution of the ethereal salt of the diamido-compound with sulphuric acid (1 H_2SO_4 to 1 of water) and zinc-dust, it is easily reduced, and on adding water a colourless substance crystallising in needles separates out. This was found to contain no nitrogen, and it was therefore supposed to be ethyl pyromellitate. A close study, however, of the substance, after v. Baeyer had observed that ethyl paradiamidoterephthalate is converted by reduction into ethyl succinosuccinate, has shown that it is identical with ethyl paradiketohexamethylenetetracarboxylate, described below.

On converting this product into ethyl quinoltetracarboxylate and into ethyl quinonetetracarboxylate, the last doubt about the complete identity of the two substances vanished.

Ethyl diamidopyromellitate is therefore reduced by means of zinc-dust and sulphuric acid according to the following reaction:—



Ethyl paradiketohexamethylene-tetracarboxylate.

Oxidising agents such as ferric chloride, platinic chloride, or sodic nitrite in acid solution, do not convert the ethereal salt of the diamido-compound into the corresponding quinone, chromic acid in acetic acid solution as well as potassic dichromate and sulphuric acid decompose it entirely. Concentrated nitric acid, however, oxidises it to the quinone.

(4.) *Ethyl Diacetyldiamidopyromellitate.*—This was obtained by heating the diamido-compound with excess of acetic anhydride at 140° for four or five hours; on adding alcohol, the new compound was in great part precipitated. After getting rid of the excess of acetic anhydride, the substance was purified by crystallisation from alcohol; it forms colourless, lustrous rhombic plates melting at 149°.

0·1161 gram substance gave 0·2342 gram CO_2 and 0·0614 gram H_2O.

	Theory for $C_6(COOC_2H_5)_4(NHAc)_2$.	Found.
C	55·00	55·01
H	5·83	5·88

The acetyl-derivative dissolves easily in acetone, chloroform, and in warm alcohol. It cannot be again resolved into its components by treating with sodium hydrate or hydrochloric acid. The same is true of many other acetyl-derivatives of amido-acids.

(5.) *Ethyl Quinonetetracarboxylate or Ethyl Quinonepyromellitate.*—On heating ethyl diamidopyromellitate with concentrated nitric acid, or with sulphuric acid and potassic nitrate, it is oxidised to the corresponding quinone. The presence of nitrous acid is detrimental, giving rise to oily bye-products. The best yield (50—55 per cent.) was obtained by the following method: 5 grams of the substance were dissolved in 40 c.c. pure concentrated nitric acid (sp. gr. 1·4) and allowed to stand in the cold for two hours. The substance dissolves at first with yellow colour and without change; soon, however, the solution becomes much darker, and the quinone begins to crystallise out in yellow needles. A slow and constant evolution of gas is noticed after the end of the first hour. It is therefore well to stir from time to time. On pouring into water, the quinone separates out completely in yellow needles. For analysis, it was crystallised twice from alcohol, when it was obtained in long, yellow needles, melting at 148—149°.

The results of the analysis agreed with the formula $C_6O_2(COOC_2H_5)_2$.

0·1375 gram substance gave 0·2756 gram CO_2 and 0·0662 gram H_2O.

	Theory.	Found.
C	54·55	54·66
H	5·15	5·35

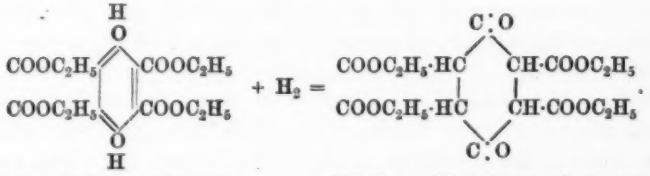
The substance is of quinone-yellow colour; it is odourless; it sublimes readily without decomposition, and unquestionably belongs to the class of true (para) quinone compounds. It is very stable in the presence of concentrated nitric acid, in which it easily dissolves. The solution, even when heated a long time, undergoes little change, and the quinone separates again completely on adding water. It is but little soluble in cold alcohol or ether; much more so in warm.

Hydroxylamine hydrochloride in neutral or acid solution reduces it almost immediately to the quinol compound. It is insoluble in cold potassic hydrate; on heating gently, however, it liquefies, turns dark-red, and then goes into solution. By using the calculated amount of potassic hydrate, it was saponified, and, strangely enough, the product obtained was dihydroxypyromellitic acid. On saponifying in acid solution with acetic acid and concentrated sulphuric acid, dihydroxypyromellitic acid also was obtained, and not as was expected pyromellitic-acid-quinone.

(6.) *Ethyl Dihydroxypyromellitate or Ethyl Quinoltetracarboxylate.*—On treating ethyl quinonetetracarboxylate with zinc-dust and acetic acid, it is reduced with great ease to the corresponding quinol-compound, $C_6(OH)_2(COOC_2H_5)_4$ [1 : 4 : 2 : 3 : 5 : 6]. This, as will become evident from what follows, has a most remarkable resemblance, in chemical as well as physical properties, to Herrmann's (*Annalen*, **211**, 327) so-called ethyl quinonedihydrodicarboxylate; the latter, according to recent results obtained by v. Baeyer (*Ber.*, **19**, 428), is to be regarded as ethyl quinolparadicarboxylate,

$$C_6H_2(OH)_2(COOC_2H_5)_2\,[1:4:2:5].$$

Of especial interest, moreover, is the action of reducing agents on ethyl quinoltetracarboxylate. It is converted in a manner analogous to the conversion of ethyl quinoldicarboxylate to ethyl succinosuccinate—to a hexamethylene-derivative or hexahydrated derivative of benzene—that is, from a tertiary to a secondary bound ring (v. Baeyer, "*Ueber Nomenclatur*," *Ber.*, **19**, 160).



Ethyl quinoltetracarboxylate. Ethyl paradiketohexamethylenetetracarboxylate.

The resulting compound, ethyl paradiketohexamethylenentetracarboxylate (*Ber.*, **19**, 160) has a remarkably deceptive resemblance in all respects to ethyl succinosuccinate. By means of bromine in carbon

bisulphide solution, it can be reconverted to ethyl quinonetetracarboxylate.

In order to reduce ethyl quinonetetracarboxylate, it is dissolved in acetic acid and zinc-dust added in small portions. The yellow solution immediately become colourless with a beautiful blue fluorescence. On adding water, the quinol compound separates out in almost colourless needles having a marked bluish tinge. For purification, it is dissolved in acetic acid and precipitated again by addition of water.

I. 0·1280 gram substance gave 0·2564 gram CO_2 and 0·0676 gram H_2O.

II. 0·1475 gram substance gave 0·2934 gram CO_2 and 0·0752 gram H_2O.

	Theory for $C_6(OH)_2(COOC_2H_5)_4$.	Found. I.	Found. II.
C	54·27	54·62	54·25
H	5·53	5·86	5·66

Ethyl quinoltetracarboxylate crystallises in pale-yellow needles having a bluish tinge. It has no sharp melting point, 127—129°. When carefully heated between two watch-glasses, it sublimes without decomposition. It dissolves easily in alcohol, ether, and acetic acid, and the solutions show a very marked, beautiful blue fluoresence. On adding a drop of ferric chloride to an alcoholic solution of the substance, a bluish-green coloration is produced.

If heated with concentrated nitric acid, it dissolves and is oxidised quantitatively to the quinone. It remains unchanged when exposed to an atmosphere of bromine for several days. It dissolves unchanged with yellow colour in dilute sodic hydrate or sodic carbonate. Concentrated sodic hydrate precipitates a deep cinnabar-red sodium salt, which is also obtained on adding sodic ethylate to a dry ethereal solution of the quinone. On heating the sodium hydrate solution, hydrolysis takes place, and the sparingly soluble sodium salt of dihydroxypyromellitic acid separates out in yellowish prisms.

Ethyl quinoneparadicarboxylate also forms a similar coloured sodium salt, and gives bluish-green coloration with ferric chloride. The solution of the substance in ether also shows the same marked blue fluorescence.

An investigation of the physical properties of ethyl quinoltetracarboxylate has shown still further the remarkable resemblance existing between these two compounds. The study of the physical properties of this substance—which certainly is one of the most

remarkable substances physically in chemistry—was begun during the last Easter vacation in the new chemical crystallographical laboratory of Professor P. Groth.

Dr. W. Muthmann reports thereon as follows:—

Ethyl Quinoltetracarboxylate.

Modification I.

Monoclinic system: $\beta = 64° 36'$.

$$a : b : c = 2{\cdot}3875 : 1 : 3{\cdot}0601.$$

Planes: $c = (001) = 0P$. $r = (\bar{1}01) = +P\infty$.
$q = (101) = -P\infty$. $m = (110) = \infty P$.

Elongation in the direction of the axis b; often in thin needles. The base never predominates but always appears as a small plane.

	Found.		Calculated.	
(110) : ($\bar{1}$10)	*49°	45′	—	—
(001) : (101)	*36	46	—	—
(001) : ($\bar{1}$01)	*68	45	—	—
(110) : (101)	68	10	68°	29′
($\bar{1}$10) : ($\bar{1}$01)	73	13	73	27

Colour, greenish-yellow. The plane of the optic axes lies in the plane of symmetry. An optical axis appears very nearly perpendicular to ($\bar{1}$01) and as a consequence no total reflection is noticeable on this face.

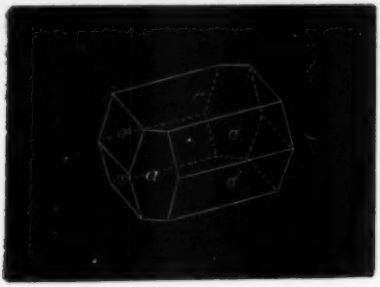
In (101) pretty strong dichroism—dark-yellow and light-yellow—noticeable; this was not perceptible in ($\bar{1}$01).

Modification II.

Monoclinic system: $\beta = 81° 53'$.

$$a : b : c = 1{\cdot}7896 : 1 : 3{\cdot}3206.$$

Planes: $c = (001) = 0P$. $0 = (111) = -P$.
$a = (100) = \infty P\infty$. $0' = (\bar{1}11) = +P$.



Thick plates in direction (001). In many of the crystals the corresponding opposite planes were not quite parallel owing to disturbances in their growth.

The angles used in the calculation of the axial ratios, &c., are the mean of 20—25 angle measurements on eight of the best crystals.

	Found.		Calculated.	
(111) : ($\bar{1}$11)	56°	43′	—	—
(111) : (1$\bar{1}$1)	111	44	—	—
($\bar{1}$11) : ($\bar{1}\bar{1}$1)	117	53	—	—
(100) : (001)	81	57	81°	53′
(001) : (111)	71	25	71	28
(001) : ($\bar{1}$11)	78	45	78	55
(100) : (111)	59	40	59	49
($\bar{1}$00) : ($\bar{1}$11)	63	21	63	28

Colour, pale-yellow. Dichroism—colourless and bright-yellow—noticeable in (001). The total reflection in (001) exactly diagonal.

In the summer, transparent crystals of the first modification alone were obtained from carbon bisulphide solution. These on heating become turbid and seem to undergo a transformation. The change begins at 111° and is complete at 115°. The product then melts, on higher heating sharply, at 133·2—133·6°.

In the colder months (April), at a temperature of about −5°, crystals of the second modification were obtained side by side with the first modification from a solution in carbon bisulphide. Modification II becomes transformed at 63·5—64° into a different modification. On cooling, this does not change back to the original again. The modification thus obtained at 64° shows a peculiar fusing point. It begins to melt at 123—124°, and thereupon a part of the substance becomes solid again and the whole melts entirely at 128·5°. On cooling and reheating, the same phenomena again appear.

Besides these two modifications, a third was observed to crystallise from the carbon bisulphide solution at very low temperatures. The

amount of material on hand has up to the present time been insufficient for the closer study of this peculiar modification.

The modifications I and II described are undoubtedly totally different from one another, and it is *not* possible by heating or fusing to convert either one into the other. There is first of all a remarkable difference in colour: I is green; II, pale-yellow. On fusing and cooling, I appears dark-yellow; II, bright-yellow. One modification crystallises in needles, the other in plates, so that it is an easy matter to separate them mechanically. When either modification thus sharply separated is dissolved in carbon bisulphide, the mixture of the two modifications side by side, like two substances totally distinct from one another, is again obtained. If these are carefully separated mechanically and the operation repeated, the same result is invariably obtained, showing a mixture of the two modifications side by side.

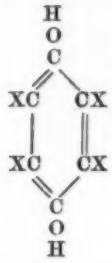
The substance, therefore, on being dissolved in carbon bisulphide (the same result is obtained on using pure dry ether) must undergo some transformation. The molecules of the substance must either possess a very peculiar tendency to arrange themselves always in two definite states of equilibrium corresponding to the two totally different crystalline forms, or, what is equally probable, certain atoms of the molecule of the substance itself must be in a perpetual unstable equilibrium, and the two modifications observed would then correspond each to a different molecular structure. Certain it is the solutions of the two modifications have exactly the same colour. The absorption-spectrum of each modification dissolved in dilute sodium carbonate solution was quantitatively determined for all parts of the spectrum, and found in both cases to be exactly the same. The data, &c., will be given later in connection with a study of the absorption-spectra of various other closely allied substances. On oxidation with concentrated nitric acid, both modifications I and II give the same perfectly homogeneous substance, the quinone melting sharply at 149°, whilst on treatment with zinc-dust and hydrochloric acid in alcoholic solution, both give the same *colourless* and perfectly homogeneous substance—the diketone compound melting at 144°.

It is worthy of note that quinol and many other derivatives of quinol or paradihydroxybenzene, as well as *paradiamido*-derivatives of benzene are dimorphous. It may be noted now that Dr. Muthmann has discovered two entirely distinct modifications of ethyl paradiamidoterephthalate (*Ber.*, **19**, 430), and measured the crystals of both forms, only one modification has as yet been found of the very closely allied ethyl paradiamidopyromellitate.

The fact that so many of the paradihydroxy-derivatives of benzene are dimorphous naturally leads one to suspect that this dimorphism

may be due to a difference in the molecular constitution of these substances.

It might be supposed that one modification corresponds to the real paradihydroxy-derivative of benzene, *e.g.*,



(X = H, $COOC_2H_5$, or any other atom or group of atoms).

and that the other modification corresponds to the pseudo- or ketone form, *e.g.*,

(X = H, $COOC_2H_5$, or any other atom or group of atoms).

The transference of the hydrogen-atoms to adjacent carbon-atoms which is assumed here, is analogous, for instance, to what takes place in the case of carbostyril, isatin, pyridone, and phloroglucin (*Ber.*, **19**, 159). In all these instances, the chemical behaviour of these substances necessitates the assumption of pseudo-forms or of the migration of the hydrogen-atom to an adjacent carbon- or nitrogen-atom. These compounds, however, have never been obtained in two different physical modifications.

If the dimorphism of the quinol compounds is due to a difference in chemical constitution, it must be possible to prove this by chemical means; the experiments thus far carried out, however, have been insufficient to settle this question.

A short time ago Nietzki and Kehrmann (*Ber.*, **20**, 613) found that quinol reacts with hydroxylamine, giving a compound $C_6H_8N_2O_2$. If the above theory is correct, this compound ought to have the formula $C_6H_8N_2O_2$ (that is, contain two more hydrogen-atoms). These experiments were repeated, but the analysis of the substance confirmed the formula given by Nietzki and Kehrmann, which seems to show that quinol is first oxidised to quinone, and then acted on by the hydroxylamine.

The study of the action of hydroxylamine on ethyl quinoltetracar-

boxylate, as well as on tetrachloroquinol, has not as yet given any positive results.

Dr. Muthmann and myself have joined to make a combined chemical and physical study of this subject. We have decided to publish here the results thus far obtained, because Hantzsch and his pupils (Hantzsch and Zeckendorf, *Ber.*, **20**, 1308, 2796; Hantzsch and Hermann, *Ber.*, **20**, 2801) in their study of ethyl quinolparadicarboxylate and its derivatives have found the same peculiar dimorphism to exist.

Hantzsch has gone further, and puts especial stress on the colour of the modifications. If the modification is colourless, he says, this corresponds to the *true* paradihydroxy-compound of benzene, as all *true* compounds of benzene must be colourless (?). If the modification is coloured, it corresponds to the ketone or quinone form, because all ketones or quinones are coloured (?).

The question of colour is, it seems to us, purely arbitrary, and does not prove anything whatever. More has hitherto been considered necessary in settling the constitution of a chemical compound.

It is very difficult to see, for instance, why ethyl quinolparadicarboxylate, which according to Hantzsch is a ketone in its *two* most stable modifications, does not under any circumstances act chemically like a ketone, but invariably like a dihydroxy-compound of benzene.

Hermann's argument (*Ber.*, **19**, 2229, 2235) that ethyl quinolparadicarboxylate forms isomorphous mixtures with ethyl succinosuccinate seems a much more powerful argument for its ketone form. On the other hand, it must be remembered that ethyl succinosuccinate acts like a dihydroxy-compound as well as like a diketone, so that it is more logical to conclude that in the isomorphous mixtures the dihydroxy modification of ethyl succinosuccinate is present.

(7.) *Dihydroxypyromellitic Acid, or Quinoltetracarboxylic Acid.*—On heating ethyl quinoltetracarboxylate with potassic hydrate, it is easily saponified; the product, dihydroxypyromellitic acid, resembles very closely paradihydroxyterephthalic acid (*Annalen*, **211**, 335).

2 grams of the ethereal salt were heated with twice the calculated amount of potassic hydrate (4 grams) on a water-bath; a dark-yellow solution with a green fluorescence was obtained. After neutralising with acetic acid, the lead salt was precipitated by means of lead acetate; the precipitate was collected, carefully washed, and then decomposed with sulphuretted hydrogen. After filtering hot from the lead sulphide and concentrating the yellowish solution, a pale-yellow substance crystallised out almost completely on cooling in four- and six-sided prisms. The substance purified by recrystallisation from water was found not to be free from ash. On adding concentrated hydrochloric acid to a hot concentrated solution, pure

dihydroxypyromellitic acid separates out almost completely in pale-yellow, broad, flat needles.

The acid, dried on an air-bath at 100°, was found to contain $1\frac{1}{2}$ mols. H_2O.

0·1227 gram substance gave 0·1706 gram CO_2 and 0·0339 gram H_2O.

	Theory for $C_6(OH)_2(COOH)_4 + 1\frac{1}{2}H_2O$.	Found.
C	38·34	37·92
H	2·87	3·07

Heated to a higher temperature (150°), the substance not only lost its water of crystallisation, but was further changed.

Dihydroxypyromellitic acid dried at 100° is of a pale-yellow colour, and dissolves sparingly in most solvents. The yellow solutions show a characteristic green fluorescence. It dissolves easily in hot water, and is precipitated therefrom by mineral acids. The aqueous solution is coloured deep blue on the addition of a few drops of ferric chloride. The colour remains unchanged for days, even when a great excess of ferric chloride is added.

When heated in a test-tube, it melts at a very high temperature, losing water, and then sublimes without leaving any residue, the sublimate, which is probably the dianhydride of the acid, crystallising in yellow, flat needles. It dissolves in dilute alcohol with yellowish-red colour and reddish-yellow fluorescence. On shaking the solution with air, a peculiar violet tinge is noticed on the sides of the test-tube. On standing, or more quickly on heating, the colour of the solution changes to the yellow tint and green fluorescence of dihydroxypyromellitic acid again.

The salts of this acid are yellow, and in solution exhibit a characteristic green fluorescence. The silver salt was more closely studied and analysed. It was obtained by adding a solution of the neutral ammonium salt to a neutral solution of silver nitrate in the cold. It separates out as a lemon-yellow flocculent precipitate. When dry, it is stable at ordinary temperature. Heated quickly on platinum foil it explodes; if heated slowly, a volatile, yellow substance sublimes.

0·2283 gram substance dried over sulphuric acid in a vacuum gave 0·1394 gram CO_2 and 0·0114 gram H_2O.

0·0562 gram substance gave 0·0338 gram silver.

	Theory for $C_6(OH)_2(COOAg)_4$.	Found.
C	16·80	16·65
H	0·28	0·55
Ag	60·51	60·14

Lead acetate throws down the lead salt as a light-yellow, flocculent precipitate; baric chloride gives the barium salt as a granular, pale-yellow precipitate. The sodium salt is especially characteristic. On heating the free acid with sodium hydrate, the sodium salt separates out in pale-yellow prisms, which are very sparingly soluble even in boiling sodium hydrate.

The oxidation of dihydroxypyromellitic acid to pyromellitic-acid-quinone, $C_6O_2(COOH)_4$, presented unexpected difficulties. Concentrated nitric acid has, in the cold, no effect on dihydroxypyromellitic acid; on heating, gently, however, the substance dissolves with a violent evolution of carbonic anhydride, and, as it would seem, is completely decomposed.

When heated gently with a solution of chromic acid, a violent evolution of gas is noticed. Potassium permanganate oxidises the acid in neutral or acid solution in the cold, but although as much as three times the calculated amount of the oxidising agent was used, much unchanged dihydroxypyromellitic acid was the only product obtained. A solution of the acid allowed to stand in the cold for days with a great excess of ferric chloride, retained the beautiful blue coloration unchanged, and much unchanged acid was found to be present. It may be mentioned here again that ethyl quinonetetracarboxylate on hydrolysis in acid or in alkaline solution invariably gives dihydroxypyromellitic acid and not the quinone.

A similar resistance towards the formation of the quinone from a paradioxy-compound was observed in the case of paradihydroxybenzoic acid $C_6H_3(OH)_2{\cdot}COOH$, and its ethyl salt. Repeated attempts were made to oxidise these substances to quinones, varying the conditions in every conceivable way. Paradihydroxybenzoic acid was found to evolve carbonic anhydride even on heating gently with such a mild oxidising agent as ferric chloride. Ethyl paradihydroxybenzoate, when treated with oxidising agents, either remained unchanged or was entirely decomposed.

Similar negative results were obtained by Brunner (*Monats. Chem.*, 1881, 464) in the case of toluquinolcarboxylic acid,

$$C_6H_2(CH_3)(OH)_2{\cdot}COOH,$$

and its ethyl salt.

Hantzsch and Loewy (*Ber.*, **19**, 26) could not convert ethyl quinolparadicarboxylate into the corresponding quinoneterephthalate, although they succeeded in obtaining another oxidation product.

(8.) *Ethyl Paradiketohexamethylenetetracarboxylate.*—The conversion of ethyl quinoltetetracarboxylate into a derivative of hexahydrobenzene or hexamethylene—that is, from a tertiary to a secondary chain of six carbon-atoms—can readily be accomplished by v. Baeyer's

method (*Ber.*, **19**, 432). To a very concentrated hot alcoholic solution of the substance (2 grams), zinc-dust (10 grams) was added, and then concentrated hydrochloric acid. The change takes place almost instantly and quantitatively. On adding water to the filtrate, a colourless substance separates out in needles: this, when purified by dissolving in a little alcohol and precipitating with water, was obtained in long, colourless needles.

The substance contains water of crystallisation, and melts therein at 94°. Heated in an air-bath at 110°, it loses its water of crystallisation, and a hard, granular mass remains, fusing at 144°.

0·1312 gram substance dried at 110° gave 0·2590 gram CO_2 and 0·0720 gram H_2O.

	Theory for $C_{18}H_{24}O_{10}$.	Found.
C	54·00	53·84
H	6·00	6·10

The anhydrous substance is very sparingly soluble in alcohol, ether, and carbon bisulphide. It separates from hot carbon bisulphide solution in beautiful, colourless needles. The solutions show a very faint but distinct blue fluorescence. The substance containing water of crystallisation, on the other hand, is easily soluble in alcohol and ether.

On adding sodium ethylate to a dry ethereal solution of the diketone compound, a colourless salt separates out at first, but on adding more sodium ethylate, this changes to a rose-coloured salt. Ethyl succinosuccinate gives exactly the same reaction.

Potassic hydrate colours the substance yellow; on diluting with water, it dissolves, forming a yellow solution, from which the substance is precipitated unchanged on the addition of an acid.

A drop of ferric chloride added to an alcoholic solution produces a cherry-red coloration. By treatment with bromine in carbon bisulphide solution, the substance is reconverted quantitatively into ethyl quinoltetracarboxylate.

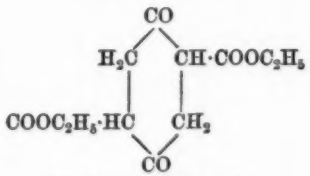
That the compound has free ketone-groups is proved by the ease with which it reacts with phenylhydrazine, hydroxylamine, and ammonic acetate. Heated over a flame with ammonic acetate, a yellow substance is obtained which dissolves in ether with a marked green fluorescence. It contains nitrogen, and melts between 115° and 120°. It is not, however, converted by treatment with bromine and concentrated sulphuric acid into ethyl diamidopyromellitate, as might be expected, from a di-imido-derivative (*Ber.*, **19**, 429). On further treatment with ammonic acetate, products melting at higher temperatures (180—200°) were obtained; these also could not be converted

into ethyl diamidopyromellitate. It was therefore considered probable that the ethylated carboxyl-groups, as well as the ketone-groups, were attacked by the ammonic acetate.

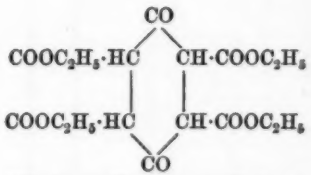
On heating an alcoholic solution of ethyl paradiketohexamethylenetetracarboxylate with phenylhydrazine (twice the calculated amount) for 10 hours at a temperature of 110—120°, in small amount, a substance crystallising in red needles is formed; as it is quite insoluble in alcohol, it is readily obtained pure. The chief products of the reaction are soluble in alcohol, and form a red, granular mixture; want of material has thus far prevented me from obtaining them in quantity sufficient to purify them for analysis. They all contain nitrogen.

The red product insoluble in alcohol shows all the properties of diphenyldipyrrazohexahydrobenzene (*Ber.*, **17**, 551, 2055), a compound which Knorr obtained by the action of phenylhydrazine on ethyl succinosuccinate. It dissolves in alkalis with purple-red colour; also in concentrated mineral acids, but is precipitated in yellow flakes on the addition of water. On treatment with sodium nitrite in acetic acid solution, a blue insoluble dye is formed. The same blue compound is produced on adding sodium nitrite to an alkaline solution, and then acidifying with dilute sulphuric acid.

The above facts suffice to show the very great resemblance between ethyl paradiketohexamethylenetetracarboxylate and ethyl succinosuccinate. This is not surprising when one reflects that the former compound is simply the ethereal salt of a dicarboxylated derivative of succinosuccinic acid.



Ethyl succinosuccinate.



Ethyl paradiketohexamethylene-tetracarboxylate.

To show the great resemblance between the derivatives obtained from ethyl succinosuccinate and those obtained from ethyl diamidopyromellitate, the following tables (pp. 458, 459) are added, showing the chief reactions of the different compounds.

The experiments on durylic-acid-quinone and pyromellitic-acid-quinone will be continued.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Bromine in CS_2 solution.
Ethyl succinosuccinate	colourless needles, m. p. 126—127°	faint blue fluorescence	cherry - red coloration	colourless, then rose-coloured salt	Ethyl paradihydroxyterephthalate.
Ethyl paradiketohexamethylenetetracarboxylate	colourless needles, m. p. 144°	faint blue fluorescence	cherry - red coloration	colourless, then rose-coloured salt	Ethyl dihydroxypyromellitate.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Zn and HCl in alcoholic solution.	Nitric acid.
Ethyl paradihydroxyterephthalate	light yellow needles or prisms, m. p. 133°	marked blue fluorescence	bluish-green coloration	deep red-coloured salt	Ethyl succinosuccinate	*no* ethyl quinoneterephthalate.
Ethyl dihydroxypyromellitate	greenish-yellow needles, m. p. 133·5°; light-yellow plates, m. p. 128·5°	marked blue fluorescence	bluish-green coloration	deep red-coloured salt	Ethyl paradiketohexamethylenetetracarboxylate	Ethyl quinonepyromellitate.
Paradihydroxyterephthalic acid	yellow plates	yellowish - green, with green fluorescence	intense blue coloration			CO_2 split off. Nitranilic acid formed.
Dihydroxypyromellitic acid	light-yellow flat needles	yellow, with green fluorescence	intense blue coloration			CO_2 split off. Decomposition.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Zn and HCl or H_2SO_4 in alcoholic solution	Nitric acid.
Ethyl paradiamidoterephthalate	gold-yellow needles, m. p. 168°, strong base	brown, with gold-yellow fluorescence			Ethyl succinosuccinate	*no* ethyl quinoneterephthalate
Ethyl diamidopyromellitate	fire-red prisms, m. p. 134°, weak base	red, with yellowish-red fluorescence			Ethyl paradiketohexamethylenetetracarboxylate	Ethyl quinonepyromellitate

XXXVII.—*Researches on the Constitution of Azo- and Diazo-derivatives.* III. *Compounds of the Naphthalene β-Series.*

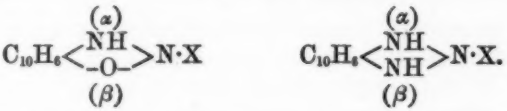
By Raphael Meldola, F.R.S., and F. J. East.

Introductory.

When diazo-salts are allowed to act on naphthalene-derivatives of the β-series, such as β-naphthol or β-naphthylamine, azo-compounds are readily formed, the N_2-group generally entering the α- (ortho) position with respect to the β-substituent. That the displaced hydrogen-atom has, at least in the majority of compounds hitherto investigated, the above-mentioned position is now placed beyond doubt by the work of numerous chemists, and there is no occasion to restate the evidence for what is now a generally received view. The azo-compounds of the naphthalene β-series, which comprise a large proportion of the azo-dyes met with in commerce, differ, however, in so many of their properties from the other azo-compounds, that it has been lately called in question whether they belong to the same class of derivatives. Thus the azo-derivatives of α-naphthol show by their phenolic character the undoubted presence of hydroxyl, whereas the corresponding β-naphthol-compounds have until recently given no distinct evidence of the presence of the hydroxyl-group. Similarly with respect to the azo-derivatives of β-naphthylamine, it was pointed out by one of the authors four years ago (Trans., 1884, 117) that these differed in many ways from the corresponding α-naphthylamine-derivatives, a fact which has since received ample corroboration from the researches of Zincke and his pupils.

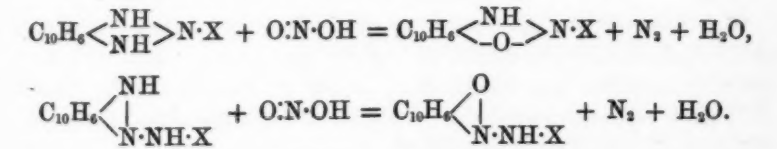
Among the points in which the azo-derivatives of β-naphthylamine differ from the corresponding α-compounds is the difference in the facility with which the two classes of compounds can be diazotised. The β-derivatives, in fact, appeared at one time to have been considered as being incapable of diazotisation, and this was especially the case with respect to the compounds obtained by the action of the diazotised nitranilines on β-naphthylamine investigated by one of the authors (see the paper referred to, Trans., 1884, 116). For the reason just stated, it was supposed that the derivatives in question did not contain an amido-group, and a formula was therefore suggested for these compounds in accordance with which they were represented as related to the azimido-compounds of Griess. An analogous view with respect to the azo-β-naphthol-compounds was about the same time put forward by Liebermann (*Ber.*, 1883, 2858),

who concluded from the circumstance that benzeneazo-β-naphthol is insoluble in aqueous alkali, that these oxyazo-β-derivatives did not contain hydroxyl. The two formulæ thus proposed as alternative to the generally received views were the following:—

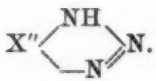


Zincke, who had previously been investigating the action of phenylhydrazine on the naphthaquinones, shortly afterwards put forward the view that the oxyazo-β-compounds were constructed on the type of hydrazides (*Ber.*, 1885, 3135; 1886, 1461; and 1887, 1169). This view of the constitution of the compounds in question appears to be maintained by Zincke (*Ber.*, 1887, 2903), and in accordance therewith the formulæ would be written—

The conclusion arrived at by one of the authors with respect to the absence of the amido-group in the β-naphthylamine azo-compounds was, as already stated, based upon negative evidence, that is, the non-diazotisable character of para- and meta-nitrobenzeneazo-β-naphthylamine. In 1886, however, the generality of this conclusion was shaken by the discovery by Nietzki and Goll (*Ber.*, 1886, 1281) that amidoazo-β-naphthalene could be converted into oxyazo-β-naphthalene by means of the diazo-reaction. This fact, although strongly suggestive of the presence of NH_2 in the compound in question, could not be taken as a complete proof, since the reaction may also be interpreted in accordance with the formula proposed by one of the authors or with that of Zincke. It is, in fact, not inconceivable that the NH-group and nitrous acid may interact according to either of the equations:—



It was suggested by one of the authors in 1884 (*Chem. News*, December 5th) that much light would be thrown on the constitution of these and other azo-compounds by investigating the products of reduction of their acetyl- or alkyl-derivatives. This method has already been extensively applied to the investigation of the constitution of the diazoamido-compounds in the series of papers communicated to the Chemical Society by one of the authors in conjunction with Mr. F. W. Streatfeild (Trans., 1886, 625; 1887, 102 and 434; *Ber.*, 1886, 3239). The investigation of the diazoamido-alkyl-derivatives is still in progress, and much work has yet to be done in this direction, as the first result of the application of the method has been the discovery of a new and quite unexpected class of cases of isomerism about which we shall have more to say shortly. In the meantime the formation of an acetyl-derivative of azimidotoluene by the action of nitrous acid on acetyl-orthotoluylenediamine observed by Boessneck (*Ber.*, 1886, 1757) shows that the constitution of the azimido-compounds, as pointed out by one of the authors (*Phil. Mag.*, June, 1887, 525), is more probably that assigned by Kekulé and Ladenburg:—



This conclusion has been recently confirmed by Nölting and Abt (*Ber.*, 1887, 2999) by the method of alkylation, so that another formula for the azo-derivatives of the naphthalene-β-series thus becomes possible:—

With respect to the oxyazo-β-naphthalene-compounds, it has been recently shown by Weinberg (*Ber.*, 1887, 3171) that benzeneazo-β-naphthol forms an ethyl-derivative, which on reduction furnishes diamidoethoxynaphthylphenyl:—

$$NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5O[C_2H_5(\beta)]{\cdot}NH_2(\alpha).$$

Weinberg justly concludes from this circumstance that the β-oxyazo-compounds contain hydroxyl. While the present research was in progress, a paper has appeared in which P. Jacobson (*Ber.*, 1888, 414) gives additional evidence in favour of the older view of the constitution of benzeneazo-β-naphthol.

This summing up of the present position with reference to the constitution of the naphthalene-β-azo-compounds will render it evident that the question as to the presence of hydroxyl and amidogen in these derivatives has been practically reopened by the experimental results recently obtained. These results must certainly be regarded as opposed

to the azimido-formula as well as to the hydrazide-formula of Zincke. Two years ago, further experiments in the direction indicated in 1884 (the method of acetylation and alkylation) were commenced by one of the authors and Mr. F. W. Streatfeild, but the work was temporarily interrupted in order to carry on other investigations. The chief conclusion arrived at in these first experiments was that the compounds obtained by nitriting the nitroazo-derivatives of β-naphthylamine in acetic acid were not, as had been at first supposed, nitroso-derivatives, although the products thus formed had neither the characters of the original compounds nor the corresponding oxyazo-compounds, nor of diazo-compounds, so that it was evident that some distinct reaction had occurred. In order to gain further insight into the course of this reaction, the research has been recently resumed, and at the same time other β-naphthaleneazo-compounds which appeared likely to throw light on the question of the constitution of these derivatives have been comprised in the investigation, the results of which we now submit to the Society.

The Action of Nitrous Acid in the Presence of Acetic Acid on the Azo-compounds obtained by the Action of Diazotised Para- and Meta-nitraniline on β-naphthylamine.

The first experiments were made with metanitrobenzeneazo-β-naphthylamine, m. p. 182° (Trans., 1884, 116).* The action of nitrous acid on this compound dissolved in glacial acetic acid varies according to the conditions of the experiment. If the substance is dissolved in a sufficient quantity of acetic acid to keep it in solution in the cold, a diazo-compound is first formed when the necessary quantity of sodium nitrite is added to the solution. On boiling, nitrogen is evolved, and on distilling off the acid, or on diluting with water, metanitrobenzeneazo-β-naphthol (Trans., 1885, 668) separates out. This compound was identified by its melting point (194°) and by the following analyses:—

I. 0·1058 gram gave 0·2558 gram CO_2 and 0·0374 gram H_2O.
II. 0·2204 „ 0·5284 „ „ 0·0753 „ „
III. 0·2298 „ 27·4 c.c. N at 15·5° C. and 759·7 mm. bar.
IV. 0·0998 „ 12 „ „ 13·5° C. „ 749 „

	Calculated for $C_{10}H_6<^{OH}_{N_2\cdot C_6H_4\cdot NO_2}$.	Found. I.	II.	III.	IV.
C.....	65·52	65·93	65·38	—	—
H.....	3·75	3·92	3·79	—	—
N.....	14·33	—	—	13·92	13·96

* In the paper above referred to, the melting point is erroneously given as 177°.

In effecting this reaction, it is necessary to use a very large quantity of acetic acid, owing to the sparing solubility of the azo-compound in this solvent, one part of the nitrobenzeneazo-β-naphthylamine requiring about 140—150 parts of glacial acid to keep it in solution in the cold. The same reaction takes place at once if one-third of this quantity of acid is used and the nitrite is added to the solution raised to just its boiling point.

The results obtained on working by either of these methods show that the reaction is in this case quite normal and analogous to the conversion of benzeneazo-β-naphthylamine into benzeneazo-β-naphthol (Zincke, *Ber.*, 1887, 2898). The chief point of interest in connection with the present method of carrying out the reaction is, that it takes place in the absence of any strong mineral acid. By representing the free diazo-compound as the first product, the reaction may be regarded as the following:—

$$C_{10}H_6\begin{matrix}<N_2\cdot C_6H_4\cdot NO_2(m)\\ N_2\cdot OH(\beta)\end{matrix} = C_{10}H_6\begin{matrix}<N_2\cdot C_6H_4\cdot NO_2(m)\\ OH(\beta)\end{matrix} + N_2.$$

We may add that the diazo-salts of metanitrobenzeneazo-β-naphthylamine are extremely unstable, and no attempts have as yet been made to isolate them.

If instead of working in the manner just described, a much smaller quantity of acetic acid is used, and the temperature is kept below 70° during the whole operation, the reaction takes an entirely different course. Under these circumstances, nitrogen is given off as before, and a substance crystallising in beautiful orange-brown scales gradually separates. After purification by crystallisation from acetic acid and then from alcohol, this compound was obtained in the form of red filamentous needles melting at 161—162°, and giving the following results on analysis:—

I. 0·1512 gram gave 0·3598 gram CO_2 and 0·0535 gram H_2O.
II. 0·1445 „ 0·3416 „ „ 0·0530 „ „
III. 0·1883 „ 19·8 c.c. N at 11·5° C. and 779·1 mm. bar.

The formula deduced from these numbers showed that the substance was the acetyl-derivative of metanitrobenzeneazo-β-naphthol:—

	Calculated for $C_{10}H_6\begin{matrix}<N_2\cdot C_6H_4\cdot NO_2\\ O\cdot C_2H_3O\end{matrix}$.	Found.		
		I.	II.	III.
C	64·44	64·89	64·47	—
H	3·85	3·93	4·07	—
N	12·53	—	—	12·82

The following are the details of the method of performing the re-

action :—One part of the nitroazoamido-compound is heated with about 70 parts of glacial acetic acid till completely dissolved, and the solution then allowed to cool down to 60—70°. The theoretical quantity of sodium nitrite is then added in the solid state in small quantities at a time, the temperature of the solution not being allowed to rise above 70°. The contents of the flask are well shaken after each addition of nitrite, and each quantity of the latter is allowed to dissolve before adding more. When all the nitrite has been added, the solution is set aside to cool, and the crystalline acetyl-derivative can be collected after 6—8 hours.

From the foregoing result, it will be seen that when metanitrobenzeneazo-β-naphthylamine is treated with sodium nitrite in the presence of acetic acid, under the conditions specified, the acetic acid takes part in the reaction :—

$$C_{10}H_6\langle^{N_2\cdot C_6H_4\cdot NO_2}_{NH_2} + 2C_2H_3O\cdot OH + NaNO_2 =$$

$$C_{10}H_6\langle^{N_2\cdot C_6H_4\cdot NO_2}_{O\cdot C_2H_3O} + N_2 + C_2H_3O\cdot ONa.$$

It is of course possible that an unstable diazo-compound is formed as an intermediate product, this compound immediately undergoing decomposition in presence of the acetic acid according to the following scheme :—

$$C_{10}H_6\langle^{N_2\cdot C_6H_4\cdot NO_2}_{N_2\cdot OH} \quad H\cdot O\cdot C_2H_3O.$$

That the acetyl-derivative has the constitution assigned to it was shown by cohobating the compound with one molecular proportion of potassium hydroxide dissolved in alcohol, when the acetyl-group was easily removed and metanitrobenzeneazo-β-naphthol (m. p. 194°) was obtained. The yield of acetyl compound is practically quantitative, and as the reaction promises to be widely applicable for the synthesis of phenolic acetates and other ethereal salts, it is proposed to extend the investigation in this direction, and to make a special study of the conditions which determine the displacement of amidogen by the $C_2H_3O\cdot O$-group by means of the diazo-reaction.

It will be of interest here to point out the analogy of this reaction to that in which phenolic alkyl-ethers are formed by the action of diazo-salts on alcohol :—

$$R\cdot N_2\cdot HSO_4 + H\cdot O\cdot C_2H_5 = R\cdot OC_2H_5 + N_2 + H_2SO_4.$$

(Fittica, *Ber.*, 1878, 1209; G. Schultz, *Ber.*, 1884 and 475; Haller, *Ber.*, 1884, 1887; Hofmann, *Ber.*, 1884, 1917; Wroblewsky, *Ber.*,

1884, 2703; Remsen, *Ber.*, 1885, 65; and *Amer. Chem. J.*, **8**, 243 and **9**, 387).

Paranitrobenzeneazo-β-naphthylamine (Trans., 1883, 430) undergoes a similar decomposition when treated with sodium nitrite in the presence of acetic acid. One part of the nitroazo-compound was dissolved in 140—150 parts of the glacial acid, and the necessary quanity of sodium nitrite added to the solution, the temperature of the latter not being allowed to rise above 70°. Paranitrobenzeneazo-β-naphthyl acetate crystallises out on cooling in beautiful red flattened needles having a slight violet reflexion. The melting point is 192—193°. After crystallisation from alcohol, in which the substance is soluble only with great difficulty, it was obtained in the form of flat orange needles having the same melting point. The following analyses were made by Mr. Streatfeild:—

I. 0·1484 gram gave 0·3510 gram CO_2 and 0·0523 gram H_2O.
II. 0·1988 „ „ 0·4694 „ „ 0·0724 „ „

	Calculated for $C_{10}H_6<\begin{matrix}N_2\cdot C_6H_4\cdot NO_2\\O\cdot C_2H_3O\end{matrix}$.	Found. I.	Found. II.
C.....	64·44	64·50	64·39
H	3·85	3·91	4·04

The acetyl-derivative, like its metanitro-isomeride, is readily decomposed by boiling for a short time with one molecular proportion of potassium hydroxide dissolved in alcohol, the acetyl being removed and paranitrobenzeneazo-β-naphthol, m. p. 249° (Trans., 1885, 662), being formed.

Acetylation of Oxyazo-β-naphthalene Compounds.

In order to ascertain whether acetyl-derivatives could be obtained by direct acetylation as well as by the diazo-reaction with acetic acid, metanitrobenzeneazo-β-naphthol (m. p. 194°) was boiled for about 12 hours with acetic anhydride and anhydrous sodium acetate. The product, after being washed with water and crystallised from alcohol, proved to be identical with the acetyl-derivative of m. p. 161—162° obtained in the manner described in the foregoing part of this paper. The acetylation of the nitroazo-compound could not be effected in less time than that specified.

Benzeneazo-β-naphthyl acetate.—In order to prepare this compound, benzeneazo-β-naphthol was boiled with acetic anhydride and dry sodium acetate for 24 hours, the acetylation not being completed in less time. The product, after being washed with water and crystallised two or three times from alcohol, was obtained in the form of

deep orange-coloured scales melting at 117°. It gave the following numbers on combustion:—

0·1520 gram gave 0·4130 gram CO_2 and 0·0679 gram H_2O.
0·2463 „ „ 20 c.c. N at 14·5° and 772·4 mm. bar.

	Calculated for $C_{10}H_6 < \begin{matrix} N_2 \cdot C_6H_5 \\ O \cdot C_2H_3O \end{matrix}$	Found.
C	74·48	74·16
H	4·82	4·93
N	9·65	9·68

It follows from these results that the azo-derivatives of β-naphthol contain one atom of hydrogen capable of being displaced by acetyl, and the experiments of Weinberg already referred to have shown that these compounds are also capable of being ethylated. In order to clear up the constitution of these derivatives, it is only necessary to ascertain whether the acetyl- or alkyl-group is attached to oxygen or nitrogen, that is, to find out whether the displaced hydrogen-atom is imidic or hydroxylic. That the latter is the case is shown by the conversion of metanitrobenzeneazo-β-naphthylamine into metanitrobenzeneazo-β-naphthyl acetate by means of the diazo-reaction with acetic acid as described in the present paper. This acetate is identical with that produced by the direct acetylation of netanitrobenzeneazo-β-naphthol, and is converted into the latter by hydrolysis. We have not yet succeeded in converting benzeneazo-β-naphthylamine into benzeneazo-β-naphthyl acetate by the diazo-reaction with acetic acid,* but since Zincke has shown that this reaction in the presence of water converts the amido-β-azo-compound into the corresponding benzeneazo-β-naphthol, the chain of evidence is so far complete. The direct proof of the constitution of these β-azo-derivatives of naphthalene will however be only forthcoming when the products of complete reduction have been studied. We have already made a large number of experiments in this direction, but have met with so many practical difficulties that we prefer to withhold the results for the present. We may state in conclusion, that the whole of the evidence thus far obtained points distinctly to the existence of hydroxyl and amidogen respectively in the β-oxyazo- and β-amidoazo-compounds of naphthalene, but we refrain from offering any opinion upon the constitution of these derivatives until more experimental evidence has been obtained.

Finsbury Technical College,
March 10th, 1888.

* Acetic anhydride cannot be used in this reaction, as it acts so energetically on benzeneazo-β-naphthylamine that complete decomposition with the formation of resinous products takes place.

XXXVIII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XII.—*The action of finely divided metals on solutions of Ferric Salts, and a rapid method for the titration of the latter.*

By Douglas J. Carnegie, B.A., Demonstrator in Chemistry, Gonville and Caius College.

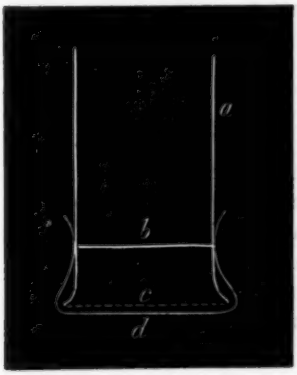
1. It is universally admitted in text-books, that of existing methods for converting ferric salts into ferrous salts prior to titration with potassium permanganate, the safest and best, though by far the slowest, method is to boil the acidified ferric solution with zinc in an inert atmosphere. The more rapid methods (excluding the stannous chloride method, which is not applicable if permanganate titration be employed) are hampered by the facts that in their employment it is difficult to determine the point of exact reduction, and excess of the reducing agent is as fatal as defect.

It seemed to me that the safest method might be so modified as at the same time to make it a rapid one, by increasing the effective surface of the zinc through the employment of zinc-dust in the place of the usual granulated zinc. While experimenting in this direction, I found that zinc-dust *instantly* reduces ferric to ferrous salt, *and this even in neutral solutions*. At the same time, if the solution is neutral, iron is precipitated partly as ferrous, partly as ferric hydroxide. In acid solutions, no iron is precipitated, but the reduction is less rapid the more free acid there is present. In every case zinc goes into solution.

2. Very rapid and accurate estimations of ferric solutions are realised by the following method:—

The bottom of a dry and narrow beaker is covered with zinc-dust, which has been sifted through fine muslin. A known volume of ferric solution, previously nearly neutralised by ammonia, is now delivered into the beaker, and shaken briskly with the zinc-dust. Finally, a known volume of dilute sulphuric acid is added, and the contents of the beaker are once more shaken. It is essential for rapid reduction that the above order be observed; the nearly neutral ferric solution must *first* be added to the zinc, *then* the acid. In order to withdraw for titration a definite volume of the ferrous solution free from particles of undissolved zinc, I make use of the "reversed filter," figured, in which *a* is a glass tube; *c*, muslin; *d*, filter-paper, held in position by an india-rubber ring, *b*. When this filter is

immersed in the beaker, the clear ferrous solution rises in it to the same level as the liquid in the beaker, and may then be withdrawn by



a pipette. The object of the muslin, *c*, is to prevent rupture of the filter-paper by the narrow end of the pipette. A titration which formerly demanded an hour or more can be executed by this method in three or four minutes with an accuracy deducible from a comparison of the following numbers selected at random from a series of titrations in which no special refinements were employed:—

25 c.c. of an acidulated ferric chloride solution reduced by iron-free magnesium required 15·3 c.c. of a decinormal permanganate solution.	25 c.c. of same solution reduced as above required 15·2 c.c. of same permanganate solution.

If one is to judge from Aldendorff's analysis of a typical specimen of zinc-dust (Fremy's *Encyclopèdie*), this substance is usually free from iron. The specimen with which I worked contained only 0·08 per cent. of iron, or rather reducing substance equivalent to 0·08 per cent. iron.

3. As to the nature of the reaction between zinc-dust and neutral ferric chloride, I was at first inclined to ascribe the efficacy of the dust in this respect to the occluded hydrogen which, as Greville Williams has shown, is always contained therein. I was all the more strengthened in this view by experiments which showed that hydrogen occluded by palladium quickly reduces ferric chloride in solution. It is interesting in this connection, coupled with the experiments of Gladstone and Tribe, to note that hydrogen occluded by platinum has no action on ferric salts.

To put this hypothesis to the proof, I heated some of the zinc-dust in a Sprengel vacuum till all the hydrogen was given off; I then

tried the action of the volatilised zinc crystals on ferric chloride. Their reducing power was unimpaired; hence I had to seek for a new explanation.

It is well known that ferric chloride in aqueous solution is in a state of partial dissociation, as is roughly represented in the equation—

$$Fe_2Cl_6 + (n + 3)H_2O \rightleftharpoons (Fe_2O_3nH_2O) + Fe_2Cl + 6HCl.$$

It might be urged that on adding zinc-dust to such a system, the hydrochloric acid would be removed from the sphere of action, with formation of zinc chloride and hydrogen, and that the nascent hydrogen would reduce the ferric chloride existing as such, while the soluble hydrated iron oxide might in virtue of this upsetting of the mobile equilibrium be simultaneously transformed into an insoluble hydrated form. According to this explanation it would follow that more iron hydroxide would be precipitated the higher the temperature at which reduction takes place, for the dissociation of ferric chloride increases with the temperature. And, indeed, experiment proved that about twice as much iron is precipitated as insoluble hydroxide when the reduction is effected at 100° as when it takes place at ordinary temperatures. But according to this explanation, one would predict the improbability of reduction if absolute alcohol were substituted for water as the medium of the change; whereas experiment shows that even under these conditions reduction readily takes place with great rise of temperature.

4. I am thus driven to the conclusion that the zinc acts merely as a dechlorinating agent, much as stannous chloride acts—

$$Fe_2Cl_6 + Zn = ZnCl_2 + Fe_2Cl_4,$$

and that the precipitate of iron hydroxides which occurs in neutral solutions is partly due to the zinc oxide which is always present in the dust to the extent of about 50 per cent., partly to the zinc hydroxide formed during the reduction by the action of water on the finely divided zinc. Zinc-dust merely effects instantaneously the dechlorination which I found zinc-foil required several hours to effect.

The change represented above is an exothermic one; the heat of formation in aqueous solution of $ZnCl_2$ [112,840] is greater than the negative thermal change in the passage from the system Fe_2Cl_6,Aq to the system Fe_2Cl_4,Aq [55,540].

5. If this explanation of direct dechlorination be valid, it seemed probable that all those metals whose chlorides have a heat of formation in aqueous solution greater than 55,540 gram-units would, in the finely-divided state, reduce ferric solutions. I have made many experiments in this direction, and I find that the following metals in

a finely-divided state reduce ferric solutions with varying degrees of rapidity:—iron, mercury, silver, aluminium, and copper, as well as zinc. Sometimes the metals were employed in the shape of foil [aluminium, copper, silver], sometimes in the state of fine division in which they are precipitated from boiling alkaline solutions of their formates, or from hot solutions of any of their salts by means of zinc-dust, followed by repeated digestion with dilute acids suited to the occasion. In the cases of aluminium and silver, it was definitely proved that no precipitation of a salt of iron occurred. This, without doubt, would be the case with all metals M″ where $M'' + H_2O = M''O + H_2$ represents an endothermic change. Platinum and gold do not reduce ferric solutions. Now, with the exception of the last two named, the heats of formation of the chlorides of all the foregoing metals are greater than 55,540. Nevertheless, the *rapidity* of reduction by a metal does not appear to be a function of the energy which runs down in the formation of its chloride, thus $[Al^2, Cl^6, Aq] = 475{,}650$, whilst $[Zn, Cl^2, Aq] =$ only 112,840; yet zinc reduces instantaneously, whilst aluminium reduces the most slowly of all the metals experimented with. But experiment showed it to be undoubtedly the case that those metals reduce the quickest which are the most readily attacked at ordinary temperatures by dilute chlorine-water. It is of interest to note that galena in a finely-divided state also reduces ferric chloride solution, whereas antimony sulphide has not this power.

6. From the whole of my experiments, I conclude that zinc-dust is practically the best reducing agent for the purpose in hand. True it is that zinc-dust may sometimes contain a little iron, and that titration with permanganate cannot be conducted in an acid solution containing zinc, but that the latter must be first removed. But, in the first place, zinc-dust contains so little iron, and so slight a solution of zinc takes place before titration by my method, that any error arising from this source is negligible. However, in the attempt to elaborate a method which would preclude *any* uncertainty on this point, I prepared zinc-dust free from zinc oxide, as recommended by Sabatier, by means of repeated digestion with dilute acid, and also by what I found to be a more rapid method, viz., by digestion with solutions of ammonium chloride and ammonia, in both cases finally drying the product on porous tiles in a vacuum. This purified zinc was shaken up with a standard ferric chloride solution *without the addition of any acid;* the ferrous solution was filtered off, acidified, and titrated; but the iron was not fully accounted for in the filtrate, so rapidly does water attack the finely-divided zinc with formation of hydrogen and zinc hydroxide; the latter precipitating solutions of iron salts in contact with it. In fact, in solutions of

several metallic salts, $MgCl_2$, $Al_2(SO_4)_3$, $Co(NO_3)_2$, $MnSO_4$, &c., finely-divided zinc very soon causes a precipitate either of the hydroxides or of basic salts of the metals present.

In the second place, even when the reduction is effected by metals which can easily be obtained absolutely free from iron, which are not oxidised by water, and which do not evolve hydrogen with dilute acids, separation from the finely-divided metal *must* always precede titration; for even silver and aluminium are attacked in feebly acid solutions by permanganate.

7. Mitscherlich (*Zeit. anal. Chem.*, **2**, 72) has stated that in the reduction of ferric solutions it is absolutely necessary that the whole of the zinc should be dissolved before titration; the reason adduced being that iron is precipitated on the surface of the zinc, and does not dissolve until the last traces of the zinc themselves disappear. If this statement be accurate, objection may be taken to my method detailed above; but I much doubt its accuracy. Experiment showed that the titre of an acidulated iron solution was independent of the time it had remained in contact with the zinc-dust. This might be explained in this special case by supposing the finely divided zinc to be practically enveloped in a protecting layer of hydrogen, but other experiments would lead me to believe that such a supposition is unnecessary. Examination of pieces of granulated zinc free from iron removed either before or after complete reduction of both hot and cold ferric solutions, always failed to give evidence of iron. Beebe's method of reducing ferric solutions (*Chem. News*, **53**, 269) would also be untrustworthy were Mitscherlich's statement correct. Without doubt the zinc in all cases becomes coated with a black deposit, which as Rodwell, Vogel, and others have shown, contains *in addition to the iron present originally in the impure zinc iself*, zinc combined with lead, sulphur, and carbon.

8. After the work of which this paper is a short account was finished, I casually came across a reference in Fremy's *Encyclopèdie* to a paper by Brown, on the reduction of ferric compounds by zinc. I have procured the paper referred to (*Iron*, 1878, 361), and find that Brown's method consists in reducing iron ores directly by fusion with *pulverised* zinc (Hobson and Sylvester had shown that at a temperature of 205° zinc becomes so brittle that it may be powdered in a mortar). Brown has also used this pulverised zinc to reduce ferric salts in acid solutions; but that his method is founded, as is the current one, on the reducing action of nascent hydrogen, and not on the direct reducing powers of the zinc, is obvious from the following quotation:—"There should be but a very small excess of sulphuric acid present, so that at the *end of an hour or two* only about half the zinc will be dissolved." Brown is also of opinion that the whole of the zinc must be dis-

solved before titration, but he does not state his grounds for that opinion.

I prepared some pulverised zinc, by Hobson and Sylvester's method, but with three different specimens of zinc. I uniformly found that they did not become brittle at 205° but at higher temperatures, and also that it was impossible thus to obtain anything approaching the fine division of zinc-dust. The pulverised zinc obtained reduced neutral ferric solutions but slowly.

In conclusion, I would express my thanks to Mr. Pattison Muir for the kindly suggestive interest he has taken in the work detailed.

ANNUAL GENERAL MEETING,

March 28th, 1888.

W. Crookes, F.R.S., President, in the Chair.

In accordance with our bye-laws it becomes my duty to lay before you the usual Annual Report on the state of the Society during the past twelve months.

As regards the number of Fellows I am happy to state that there is no sign of falling off.

The following table shows the present state of the Society :—

Number of Fellows (March 31st, 1887)		1477
Since elected and paid admission fees.....		109
		1586
Deceased.....	11	
Withdrawn.....	11	
Removed on account of arrears	30	
	—	52
Present number of Fellows		1534
Increase		57
Number of Foreign Members (March 31st, 1887).....	31	
Deceased (J. B. Boussingault).....	1	
	—	30
Newly elected.....		7
Present number of Foreign Fellows		37

Our losses by death which include several well-known names are :—Professor C. L. Bloxam; J. B. Boussingault (foreign member), Patrick Duffy; J. J. Field; A. M. Graham; Dr. T. S. Humpidge; James Millar, A. Muter; H. H. MacMunns; W. B. Ritchie; Dr. Arthur Phillips; G. B. Sweeting; and A. E. Wilson.

11 Fellows have withdrawn :—L. M. Deane; H. W. Eve; G. F. Dowdeswell; G. Gladstone; Hugh R. Mill; Ed. Packard; T. A. Rickard; B. M. F. Rogers; C. A. Stitt; J. E. Tuit; and J. C. Wright.

The following Fellows have been removed on account of arrears :—Harry Allen; A. W. Bickerton; G. E. Barker; Dr. H. C. Bartlett; Benjamin Browning; G. E. Basu; C. N. Betts; T. J. Barr; R. D.

Courtney; Thomas Donnelly; W. T. H. Elsey; H. W. Fenner; Wm. Fox; Thos. Gibbs; G. A. George; Chas. Gillett; W. E. Heathfield; E. A. Harris; Edwin Lapper; R. T. Matthews; Alexr. Noble; Arthur Ness; O. Davies Owen; J. A. Ogilive; Thos. Palmer; Matthew Percy; J. Schweitzer; Sidney Trivick; Rev. W. G. Whittam; and Wm. Wilson.

There are 88 original papers in the Journal this year (1887), occupying 871 pages, as against 85 papers of 865 pages last year. The Abstracts this year occupy 1159 pages, as against 1088 in 1886. The number of Abstracts is 2277, as against 2164, the average of the five years preceding.

108 Papers have been communicated to the Society during the session—10 fewer than in the previous session; but if we look through the Proceedings we see that not a few of the papers have been of exceptional interest and value, and that a number of important questions have been brought forward for discussion during the year. This view is confirmed by the fact that the Transactions contain a greater number of papers than any previous years.

It is again our agreeable duty to make the triennial award of the medal founded by our highly esteemed friend and Fellow, Dr. Longstaff.

Most gentlemen here present are aware that, according to the stipulations of the giver, this medal is intended as a mark of recognition of the labours of men engaged in chemical research. Before divulging the name of the distinguished chemist to whom the Council propose the medal this year should be awarded, you will, I am sure, cordially join with me in congratulating Dr. Longstaff that, although so near the eve of his 89th birthday, he is still hale and hearty, and in expressing the hope that he may long be spared to our Society.

The medal this year is conferred on Dr. W. H. Perkin, F.R.S., a past President of our Society.

Doubtless you are all aware that Dr. W. H. Perkin has devoted a great portion of his life to an interesting and delicate department of industrial chemistry, and that he has gallantly upheld our character for indomitable scientific enterprise. He has now retired from active business, but with no intention of resting on his oars. He carries into his private laboratory the same undaunted spirit of inquiry, and devotes his well-earned leisure to diligent and difficult research.

It is not often that an opportunity such as that which has fallen to Dr. Perkin's lot is so fully made use of, and that one who has been engaged in industrial pursuits undertakes a research of such magnitude as that of which Dr. Perkin first gave an account to the

Society in 1884 (Trans., pp. 421—579), and which it is known has since wholly engaged his attention.

Dr. Perkin,—

I feel it a privilege that to my lot it has fallen to present to you the Longstaff Medal in recognition of your interesting and important researches "On the Magnetic Rotary Polarisation of Compounds in Relation to their Chemical Constitution." I hope that further examples of your investigations on this subject are in store for us, and that your example may stimulate us all, and especially the younger Fellows of the Society, to increased zeal and devotion in the extension of our Science.

Our library, thanks in great measure to the Library Committee, has had many additions to its shelves during the year. The subjoined table shows the increase.

	Additions in 1887-8.	Present state.
Volumes of systematic works	169	2,780
Volumes of journals	172	5,119
Volumes of duplicate journals for circulation.....	42	941
Pamphlets	12	1,410
	395	10,250

The expenditure under this head for the current year is £129.

The following are the titles of the papers which have been communicated to the Society since April 7th, 1887.

Papers contributed to the Chemical Society between March 30th, 1887, and March 28th, 1888.

April 7th.

I. "Researches on the Constitution of Azo- and Diazo-derivatives. II. Diazoamido-compounds (*continued*):" by R. Meldola, F.R.S., and F. W. Streatfeild.

II. "Conjugated Sulphates and Isomorphous Mixtures of the Copper-magnesium-group:" by P. C. Roy, B.Sc.

III. "Suboxide of Silver, Ag_4O:" by G. H. Bailey and G. J. Fowler.

IV. "Action of Trimethylene Bromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate and Acetonedicarboxylate:" by W. H. Perkin, Jun., Ph.D.

April 21st.

V. "The Atomic Weight of Gold:" by T. E. Thorpe, F.R.S., and A. P. Laurie, B.A.

VI. "The Atomic Weight of Silicon:" by T. E. Thorpe, F.R.S., and J. W. Young, B.A.

VII. "Note on Substitution in the Benzene Nucleus:" by H. Foster Morley.

VIII "Reply to the Foregoing Note:" by Henry E. Armstrong, F.R.S.

May 5th.

IX. "A Contribution to the Study of Well Water:" by R. Warington, F.R.S.

X. "Crystals in Basic-Converter Slag:" by J. E. Stead and C. H. Ridsdale.

XI. "Note on the Influence of Temperature on the Heat of Dissolution of Salts in Water:" by William A. Tilden, D.Sc., F.R.S.

XII. "The Distribution of Lead in the Brains of two Factory Operatives Dying Suddenly:" by A. Wynter Blyth.

XIII. "Researches on Silicon Compounds and their Derivatives. A New Chlorobromide of Silicon:" by J. Emerson Reynolds, M.D., F.R.S.

May 19th.

XIV. "The Formation of Hyponitrites:" by W. R. Dunstan and T. S. Dymond.

XV. "Ozone from Pure Oxygen:" by W. A. Shenstone and J. Tudor Cundall.

XVI. "The Volumetric Relations of Ozone and Oxygen: A Lecture Experiment:" by W. A. Shenstone and J. Tudor Cundall.

XVII. "The Thermal Phenomena of Neutralisation and their bearing on the Nature of Solution and the Theory of Residual Affinity:" by S. U. Pickering.

XVIII. "The Action of Metallic Alkylates on Mixtures of Ethereal Salts and Alcohols:" by T. Purdie, Ph.D., B.Sc.

June 2nd.

XIX. "The Equivalent of Zinc:" by Lieut.-Colonel H. C. Reynolds, late R.E., and Professor W. Ramsay.

XX. "The Magnetic Rotation produced by Chloral, Chloral

Hydrate, and Hydrated Aldehyde:" by W. H. Perkin, Ph.D., F.R.S.

XXI. "Note on a New Class of Voltaic Combinations in which Oxidisable Metals are replaced by Alterable Solutions:" by C. R. Alder Wright and C. Thompson.

XXII. "The Composition of Prussian Blue and Turnbull's Blue:" by Edgar F. Reynolds.

XXIII. "Phlorizin:" by E. H. Rennie, D.Sc.

XXIV. "Further Notes on the Chemical Action of *Bacterium aceti*:" by Adrian J. Brown.

XXV. "Note on the Cellulose formed by *Bacterium xylinum*:" by Adrian J. Brown.

XXVI. "The Oxidation of Ethyl Alcohol in the Presence of Turpentine:" by C. E. Steedman.

June 16th.

XXVII. "A Study of the Thermal Properties of a Mixture of Ethyl Alcohol and Ethyl Oxide:" by W. Ramsay, Ph.D., and Sydney Young, D.Sc.

XXVIII. "Derivatives of Hydrindonaphthene and Tetrahydronaphthalene:" by W. H. Perkin, Jun., Ph.D.

XXIX. "The Synthetical Formation of Closed Carbon-chains in the Aromatic Series:" by F. S. Kipping, B.Sc., Ph.D.

XXX. "The Product of the Action of Ethylene Bromide on Ethylic Acetosodacetate:" by P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

XXXI. "Derivatives of Pentamethylene:" by H. G. Colman, B.Sc., and W. H. Perkin, Jun., Ph.D.

XXXII. "The Synthesis of Hexamethylene-derivatives:" by P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

XXXIII. "An Attempt to Synthesise Heptamethylene-derivatives:" by P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

XXXIV. "The Composition of Shale-spirit:" by A. K. Miller, Ph.D., and T. Baker, B.Sc.

XXXV. "The Magnetic Rotatory Power of the Ethyl Salts of Maleic and Citraconic Acids and their Isomerides:" by W. H. Perkin, Ph.D., F.R.S.

XXXVI. "The Temperature at which various Sulphates undergo Decomposition:" by G. H. Bailey, D.Sc.

XXXVII. "The Reaction between Sulphites and Nitrites of Metals other than Potassium:" by Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S.

XXXVIII. "The Action of Acetyl Chloride on Acetoximes:" by Victor Meyer and A. W. Warrington, B.Sc.

XXXIX. "Sulphinic Compounds of Carbamide and Thiocarbamide:" by George McGowan.

XL. "Anacardic Acid:" by Dr. S. Ruhemann and S. Skinner, B.A.

Received during the recess and Printed in the Transactions.

XLI. "Note on an improved form of Apparatus for the Separation of Iodine, Bromine, and Chlorine:" by M. Dechan, F.C.S.

XLII. "Notes on Anhydro-bases. I. Ethenyltriamidonophthalene:" by R. Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

XLIII. "Dibenzyl Ether:" by C. W. Lowe.

XLIV. "On Aluminium in the Ashes of Flowering Plants:" by Hikorokuro Yoshida, F.C.S.

XLV. "Some Ethereal Salts of the Vanadium Acids:" by John A. Hall.

XLVI. "The Compounds of Ethyl Alcohol with Water:" by D. Mendeléeff.

XLVII. "Isomeric Change in the Phenol Series. (Second Notice):" by Arthur R. Ling.

XLVIII. "The Effects of Dilution and the Presence of Sodium Salts and Carbonic Acid on the Titration of Hydroxylamine by Iodine:" by Tamemasa Haga.

XLIX. "The Action of Light on the Hydrides of the Halogens in Presence of Oxygen:" by Arthur Richardson, Ph.D.

L. "Note on the Influence of Liquid Water in promoting the Interaction of Hydrogen Chloride and Oxygen on Exposure to Light:" by Henry E. Armstrong, F.R.S.

LI. "The Synthetical Formation of Closed Carbon-chains. Part I (*continued*). Trimethylenedicarboxylic Acid:" by W. H. Perkin, Jun., Ph.D.

November 3rd.

LII. "Note on the Atomic Weight of Gold:" by T. E. Thorpe, F.R.S., and A. P. Laurie.

LIII. "The Interaction of Zinc and Sulphuric Acid:" by M. M. Pattison Muir and R. H. Adie.

LIV. "Note on Safety Taps:" by W. A. Shenstone.

LV. "Note on Guthrie's Compound of Amylene with Nitrogen Peroxide:" by A. K. Miller, Ph.D.

LVI. "The Dehydration of Metallic Hydroxides by Heat, with Special Reference to the Polymerisation of the Oxides and to the Periodic Law:" by Professor Carnelley, D.Sc., and Dr. James Walker.

LVII. "The Bromination of Naphthalene β-Sulphonic Acid:" by G. Stallard.

LVIII. "The Constitution of the Three Isomeric Pyrocresols:" by W. Bott, Ph.D.

LIX. "Preliminary Note on certain Products from Teak:" by R. Romanis.

November 17th.

LX. "Zinc-copper and Tin-copper Alloys:" by A. P. Laurie.

LXI. "The Halogen Substituted Derivatives of Benzoylmalonic Acid:" by C. M. Stuart, M.A.

LXII. "Note on a Modification of Traube's Capillarimeter:" by H. S. Elsworthy.

LXIII. "The Formation of Hyponitrites: a Reply:" by Edward Divers, M.D., F.R.S.

LXIV. "Reply to the foregoing Note:" by W. R. Dunstan.

December 1st.

LXV. "The Alleged Existence of a Second Nitroethane:" by W. R. Dunstan and T. S. Dymond.

LXVI. "An Extension of Mendeléeff's Theory of Solution to the Discussion of the Electrical Conductivity of Aqueous Solutions:" by Holland Crompton.

LXVII. "Note on Electrolytic Conduction and on Evidence of a Change in the Constitution of Water:" by Henry E. Armstrong, F.R.S.

LXVIII. "Bismuth Iodide and Bismuth Fluoride:" by B. S. Gott and M. M. Pattison Muir.

LXIX. "The Action of Hydrogen Sulphide on Arsenic Acid:" by B. Brauner, Ph.D., and F. Tomiček.

LXX. "Note on the Constitution of Mairogallol:" by C. S. S. Webster.

December 15th.

LXXI. "An Apparatus for Comparison of Colour-tints:" by Alfred W. Stokes.

LXXII. "The Alloys of Copper and Antimony and of Copper and Tin:" by E. J. Ball, Ph.D.

LXXIII. "The Constitution of the so-called mixed Azo-compounds:" by Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

LXXIV. "The Interpretation of Absorption-spectra:" by G. H. Bailey.

LXXV. "The Reduction of Potassium Dichromate by Oxalic Acid:" by C. H. Bothamley.

LXXVI. "The Reduction of Chlorates by the Zinc-copper Couple:" by C. H. Bothamley and G. R. Thompson.

LXXVII. "Preliminary Notice on the Oxidation of Oxalic Acid by Potassium Dichromate:" by Emil A. Werner.

LXXVIII. "Isomeric Change in the Naphthalene Series. No. 1:" by Henry E. Armstrong, F.R.S.

LXXIX. "Isomeric Change in the Naphthalene Series. No. 2. Ethoxynaphthalenesulphonic Acid:" by E. G. Amphlett and Henry E. Armstrong, F.R.S.

LXXX. "Isomeric Change in the Naphthalene Series. No. 3. β-Chloronaphthalenesulphonic Acids:" by Henry E. Armstrong, F.R S., and W. P. Wynne.

LXXXI. "Isomeric Change in the Naphthalene Series. No. 4. α-Haloidnaphthalenesulphonic Acids:" by Henry E. Armstrong, F.R.S., and S. Williamson.

LXXXII. "The Sulphonation of Naphthalene:" by Henry E. Armstrong, F.R.S., and W. P. Wynne.

January 19th, 1888.

LXXXIII. "Morindon:" by T. E. Thorpe, F.R.S., and W. J. Smith, M.B.

LXXXIV. "Manganese Trioxide:" by T. F. Thorpe, F.R.S., and F. J. Hambly.

LXXXV. "Note on Chatard's Process for the Estimation of Small Quantities of Manganese:" by T. E. Thorpe, F.R.S., and F. J. Hambly.

LXXXVI. "Contributions to the Theory of the Vitriol-chamber Process:" by G. Lunge, Ph.D.

February 2nd.

LXXXVII. Lecture. "The Range of Molecular Forces:" by A. W. Rücker, M.A., F.R.S.

LXXXVIII. "A New Method of obtaining Monohydrazides of α-Diketones:" by F. R. Japp, F.R.S., and F. Klingemann, Ph.D.

LXXXIX. "The Formation of Dihydrazides of α-Diketones:" by F. R. Japp, F.R.S., and F. Klingemann, Ph.D.

XC. "The Action of Phenylhydrazine on an Unsaturated γ-Diketone:" by F. R. Japp, F.R.S., and G. N. Huntly.

XCI. "The supposed Identity of Rutin and Quercitin:" by E. Schunck, Ph.D., F.R.S.

XCII. "The Composition of Bird-lime:" by E. Divers, M.D., F.R.S., and M. Kawakita, M.E., F.C.S.

February 16th.

XCIII. "Chemical Investigation of Wackenröder's Solution and Explanation of the Formation of its Constituents:" by H. Debus, Ph.D., F.R.S.

XCIV. "Potilizin's Law of Mutual Displacement of Chlorine and Bromine:" by T. E. Thorpe, F.R.S., and J. W. Rodger.

XCV. "A Gasometric Method of Determining Nitrous Acid:" by P. F. Frankland, Ph.D.

XCVI. "The Action of some Specific Micro-organisms on Nitric Acid:" by P. F. Frankland, Ph.D.

XCVII. "The Action of Phosphorus Pentachloride on Salicylaldehyde:" by C. M. Stuart, M.A.

XCVIII. "Some Interactions of Nitrogen Chlorophosphuret:" by Ward Couldridge, B.A.

XCIX. "Action of Alcohols on Ethereal Salts in presence of small quantities of Sodic Alkylate:" by T. Purdie, Ph.D., B.Sc., and W. Marshall, B.Sc.

C. "Note on the Densities of Cerium Sulphide Solutions:" by B. Brauner, Ph.D.

March 1st.

CI. "The Origin of Colour and the Constitution of Colouring Matters:" by H. E. Armstrong, F.R.S.

CII. "Researches on Chromorganic Acids. Part II. Certain Chromoxalates of the Red Series:" by E. A. Werner.

March 15th.

CIII. "Note on Benzyldithiourethane:" by A. E. Dixon.

CIV. "The Nature of Solutions as elucidated by the Heat evolved on their Dilution. Part I. Calcium Chloride:" by S. U. Pickering.

CV. "The Action of Thiocyanates on Aldehyde Ammonias:" by A. E. Dixon.

CVI. "Carboxy-derivatives of Quinone:" by J. U. Nef.

CVII. "The Action of Acetone on Ammonium Salts of Fatty Acids in presence of Dehydrating Agents:" by S. Ruhemann and D. J. Carnegie.

CVIII. "A Method of Estimating Nitrites either alone or in presence of Nitrates and Chlorides:" by T. Cuthbert Day.

The condition of the Journal during the past year, as compared with the previous four years, is shown in the following table:—

	1883.	1884.	1885.	1886.	1887.
General and Physical Chemistry..	205	237	331	235	271
Inorganic Chemistry.....	189	189	191	223	242
Mineralogical Chemistry	204	192	201	223	180
Organic Chemistry	739	939	1047	1056	1045
Physiological Chemistry.....	73	118	142	100	100
Chemistry of Vegetable Physiology and Agriculture.....	163	324	218	160	123
Analytical Chemistry	195	256	337	289	316
Technical Chemistry.....	212	286	280	66*	—
Total.....	1980	2541	2747	2352	2277
Papers in Transactions.....	63.	57.	85.	85.	88.

I now turn to a subject of no small practical importance. During the past year the cost of our Journal amounted to the very large sum of £2116. It is to be expected that as the number of Papers offered to the Society multiplies—as it surely will—and as the number of Papers to be abstracted augments, the cost will become even greater. Our publication is of such supreme importance to chemical science in this country, that the Society is not likely to shrink at necessary expenditure. But I am impelled to refer to a question which ere long must be seriously considered, not only by us, but by scientific societies generally, viz., how far it is desirable that the same Paper should be published in more than one Journal. Our bye-laws only provide that authors shall not be at liberty, save by permission of the Council, to publish *in English* papers they have communicated, until such Papers, or abstracts of them, have either appeared in the Journal of the Society or have been returned to the writer.

It must be taken for granted in this time of culture that a paper published in English, French, or German is thus made known to the

* The Technical Division was discontinued after the April number, 1886.

entire scientific world, and, in the case of a Paper published in full in one of these three languages, it is unnecessary to give triple repetitions; an abstract of the essential facts, observations, and conclusions would be all sufficient. Some such curtailment will probably find favour, not only as a means of diminishing the cost of publication to individual societies, but also because it will put an end to the grievance undoubtedly felt by subscribers to scientific journals, of paying more than once for the same set of facts.

With this suggestion I leave the special concerns of the Chemical Society of London and turn to the general position of Chemical Science.

On occasions like the present not a few of my predecessors have laid before the Society able and instructive surveys of the progress of chemical research, discovery, and invention. For two reasons I find myself debarred from following their example.

Of late we have been favoured with such plentiful summaries of advances in every department of Science that I feel unwilling to add to the number, lest I might be accused of producing an *Ilias post Homerum*.

And secondly, although a great quantity of sound and useful work has indeed been done since our last anniversary, yet with two exceptions—I fear I must say incomplete exceptions—we have not witnessed the dawn of any epoch-making, far-reaching discovery which opens out new and tempting prospects of truth. The two exceptions which I have ventured to call partial or incomplete, because they have not yet been fully verified, are the researches of Messrs. Krüss and Nilson on the so-called rare earths, and the investigations of Professor Grünwald, of Prague. The result reached by Professor Grünwald in his mathematical discussion on certain spectral revelations seems at least to foreshadow the conclusion that hydrogen, oxygen, carbon, and magnesium are not simple bodies, but compounds. If the phenomena he records admit of no other explanation, and if no unexpected source of error is detected, we may consider ourselves to be within measurable distance of a truly "new chemistry." But here time must decide. Objections already have been raised to the conclusions of Professor Grünwald, and we are forewarned we must not allow ourselves to be carried away by our hopes and our sympathies.

To one event I must beg to draw particular attention,—the tardy justice accorded to Mr. J. A. R. Newlands, the painstaking discoverer of the periodic law of the Chemical Elements. Of the importance of this law it is utterly needless to enlarge. It has been universally accepted as a most valuable generalisation, as the grandest step in theoretical

chemistry within the last quarter of a century. Mr. Newlands formulated and published this law in all its main features as early as 1864 and 1865, and was only ridiculed for his pains; yet four or five years later, when Professor Mendeléeff announced the same idea it was received as an original discovery. Original it was in the sense that Professor Mendeléeff was perfectly ignorant of what had been done by Newlands. The strangest thing in this curious history is the fact that in 1882 the Royal Society awarded "Davy Medals" to Professors Mendeléeff and Lothar Meyer, wholly ignoring the prior claims of Mr. Newlands. By degrees, however, the truth became known; and the prior claim of Mr. Newlands was admitted in Miller's *Elements* in 1878, whilst Dr. Tilden accepted it in his *Chemical Philosophy* in 1880, and Dr. Gladstone in his Presidential Address to the Chemical Section of the British Association in 1883. Mr. Newlands reprinted his original papers on this subject in 1884, giving the date of each paper. At length, in November last, better late than never, he received from the Royal Society the well-earned award of the Davy Medal. It would be unpardonable to overlook the energetic action of Professor Frankland in bringing about the recognition of Mr. Newlands' claims. He drew up a lucid and compact statement of the case, with all the necessary evidence, and appended the opinions, published and written, of many of the most eminent chemists.

Now this episode in the history of chemical discovery appears to me to convey a lesson worth noting. We see that it is possible for an important discovery, even after full and formal publication, to be so thoroughly overlooked and forgotten, that when the same idea some years later is evolved by another and independent inquirer it passes as a striking and novel revelation.

Other occupants of the chair I now have the honour to fill have of late years discussed the position and prospects of scientific, technical, and especially of chemico-technical education. This is, doubtless, a most weighty subject. Seeing the multitude of chemical manuals we have produced, the schools and colleges and classes we have opened, and in particular the examinations we have instituted, we may fairly ask whether our returns of chemical discoveries and inventions are commensurate with all this stir and activity. Our chemical industries, we admit, are by no means in a satisfactory position. We know what systems of training prevail in the countries whose competition we have most cause to fear. We are perfectly aware in what respects these systems differ from our own. But, I may ask, what probability is there, after gleaning hints from our rivals, that we shall lay aside, or even modify, the plans we have taken up and so doggedly follow.

I cannot help quoting here the opinion of an eminent writer in the

Guardian:—"And yet man, who is so wise and good that he is always saying, like King Alphonso of Castile, 'Had we been consulted on the creation of the world we could have arranged things better,' has invented competitive examination, which means suffering and pain for all, without even a compensatory 'survival of the fittest' or improvement of the race."

I must notice an unsatisfactory feature in our schools and colleges, to which Mr. Goschen has recently called attention in his inaugural address as Lord Rector of the University of Aberdeen. It is not a flaw in our curriculum or in our methods of teaching, but something more deeply seated and less easily remedied. It is the little intellectual interest taken by the students in their studies. Mr. Goschen tells us of the abusive epithets applied in our schools and colleges to pupils who, "not content with doing their work, commit the heinous offence of being absorbed in it."

Now, in this country we have scientific men unequalled in the pure, devoted love of truth, to whom discovery is its "own exceeding great reward." Among the general run of our pupils and students there is, however, little of this enthusiastic temper, and it is, perhaps, on this very account that English educationists think it necessary to offer the stimulus of prizes and certificates, together with other accessories of the competitive system. But do not all these devices tend in the long run to increase that lack of intellectual interest which Mr. Goschen deplores, and are they not sorry substitutes for enthusiasm?

In close connection with the point just discussed there is another subject to which attention may usefully be drawn. I mean the degree of public estimation which chemistry at present enjoys. In his late Presidential Address delivered before the British Association, Sir Henry Roscoe remarked that science was less respected in Britain than in other civilised countries. A variety of facts lead me to suspect that chemistry in this sense is exceptionally unfortunate. For instance, until lately, two of the subjects for the matriculation examination at the University of London were "Natural Philosophy and Chemistry." Recently, by one of those odd alterations so often made in the curriculum of our institutions of higher education, this is changed. The subjects now demanded are—mechanics, which is compulsory for all, and, at option, one of three subjects, chemistry, or one of two departments into which physics is divided. Thus chemistry is no longer deemed indispensable!

It is to be regretted, also, that in the course adopted somewhat recently by certain of the licensing bodies of the medical profession with regard to the requirements of preliminary training in natural science, the candidate is now no longer required to study these branches in a college or school with recognised facilities for chemical

or other natural science teaching, but may obtain that instruction from any person. At first sight this may appear to be a broad and liberal measure, but on reflection it is easy to see how such action on the part of licensing bodies is a direct encouragement of the pernicious system of "cram."

It is well known that some of our public schools had begun to introduce physics and chemistry into their ordinary courses, and that other schools were preparing to follow their example. But no inconsiderable check has been given to this reasonable movement by certain changes introduced at the Military School of Sandhurst, and by others about to be adopted in the school for the Royal Engineers and Artillery at Woolwich. According to the new code, whilst as many as 3000 marks each can be earned in Latin, French, and German, and in "compulsatory" and "optional" mathematics, the utmost possible number to be gained in physics and chemistry, which rank as "second class," is 2000 each! Hence the study of these subjects, which are not made compulsory, is heavily handicapped. Even youths possessing exceptional taste and ability for physical science, if they select such subjects, must either fail altogether, or come out lower in the successful list than if they they had confined themselves to languages and mathematics. Hence physics and chemistry are much more rarely taken up. Nor does the mischief end here. The public schools which prepare boys for the admission examinations at Sandhurst and Woolwich will of course pay less attention to chemistry and physics, and may not impossibly feel inclined to drop them altogether. As *Nature* puts it:—"Good work in science pays less well than mediocrity in other subjects. The new regulations lower the standard of school work by constantly withdrawing from the science classes a large proportion of the best students." If the new regulations should be introduced at Woolwich, as is threatened, it will be somewhat farcical to speak of the Engineers and the Artillery as the "scientific branches" of the service.

Elements and Meta-Elements.

Permit me, gentlemen, now to draw your attention for a short time to a subject which concerns the fundamental principles of chemistry, a subject which may lead us to admit the possible existence of bodies which, though neither compounds nor mixtures, are not elements in the strictest sense of the word;—bodies which I venture to call "meta-elements."

To explain my meaning it is necessary for me to revert to our conception of an element. What is the criterion of an element? Where are we to draw the line between distinct existence and identity?

No one doubts that oxygen, sodium, chlorine, sulphur are separate elements; and when we come to such groups as chlorine, bromine, iodine, &c., we still feel no doubt, although were degrees of "elementicity" admissible—and to that we may ultimately have to come—it might be allowed that chlorine approximates much more closely to bromine than to oxygen, sodium or sulphur.

Again, nickel and cobalt are near to each other, very near, though no one questions their claim to rank as distinct elements. Still I cannot help asking what would have been the prevalent opinion among chemists had the respective solutions of these bodies and their compounds presented identical colours, instead of colours which, approximately speaking, are mutually complementary. Would their distinct nature have even now been recognised?

When we pass further and come to the so-called rare earths the ground is less secure under our feet. Perhaps we may admit scandium, ytterbium, and others of the like sort to elemental rank; but what are we to say in the case of praseo- and neo-dymium, between which there may be said to exist no well-marked chemical difference, their chief claim to separate individuality being slight differences in basicity and crystallising powers, though their physical distinctions as shown by spectrum observations are very strongly marked? Even here we may imagine the disposition of the majority of chemists would incline towards the side of leniency, so that they would admit these two bodies within the charmed circle. Whether in so doing they would be able to appeal to any broad principle is an open question.

If we admit these candidates, how in justice are we to exclude the series of elemental bodies or meta-elements made known to us by Krüss and Nilson? Here the spectral differences are well marked, whilst my own researches on didymium show also a slight difference in basicity between some at least of these doubtful bodies. In the same category must be included the numerous separate bodies into which it is probable that yttrium, erbium, samarium, and other "elements"—commonly so-called—have been and are being split up. Where then are we to draw the line? The different groupings shade off so imperceptibly the one into the other that it is impossible to erect a definite boundary between any two adjacent bodies and to say that the body on this side of the line is an element, whilst the one on the other side is non-elementary, or merely something which simulates or approximates to an element. Wherever an apparently reasonable line might be drawn it would no doubt be easy at once to assign most bodies to their proper side, as in all cases of classification the real difficulty comes in when the border-line is approached. Slight chemical differences of course are admitted, and, up to a certain

point, so are well-marked physical differences. What are we to say, however, when the only chemical difference is an almost imperceptible tendency for the one body—of a couple or of a group—to precipitate before the other? Again, there are cases where the chemical differences reach the vanishing point, although well-marked physical differences still remain. Here we stumble on a new difficulty: in such obscurities what is chemical and what is physical? Are we not entitled to call a slight tendency of a nascent amorphous precipitate to fall down in advance of another a "physical difference?" And may we not call coloured reactions depending on the amount of some particular acid present and varying according to the concentration of the solution and to the solvent employed, "chemical differences?" I do not see how we can deny elementary character to a body which differs from another by well-marked colour- or spectrum-reactions, whilst we accord it to another body whose only claim is a very minute difference in basic powers.

Having once opened the door wide enough to admit some spectrum differences, we have now to enquire how minute a difference qualifies the candidate to pass? I will give instances from my own experience of some of these doubtful candidates.

1. Two closely allied bodies* differ slightly in basic powers and more decidedly also in their spectrum reactions; are they distinct entities? Probably yes.

2. Two bodies† have no distinct spectrum reaction, and differ in basicity so slightly that their separation has hitherto proved to be impossible; but they differ decidedly in the colour of their oxides. Are they different? I should in this case also say "yes."

3. Two bodies‡ obtained from different minerals have no recognisable chemical difference, but there is a strong line in the phosphorescent spectrum of one which is absent in the other. What are we to say in this case?

4. An earth§ separated with enormous difficulty from its associates has a certain very definite phosphorescent spectrum. The addition of another body greatly intensifies one or more of the lines of the spectrum of the earth so separated, while upon the other lines in the

* Erbium and holmium; erbium and yttrium; samarium and didymium, &c.

† The white and yellow components of cerium (*Phil. Trans.*, **176** (1885), 704).

‡ Yttrium from samarskite gives the Sδ line, whilst in that from gadolinite this line is absent (*Proc. Roy. Soc.*, **40** (1886), 502—509). The reputed Yα of M. de Marignac contains all the phosphorescent lines of the old yttrium spectrum except the line of Gδ (*Proc. Roy. Soc.*, **40** (1886), 236).

§ The phosphorescent spectra of yttrium and samarium are modified by the addition of various earths in the way here mentioned. Samarium affects the alumina spectrum in a similar manner (*Proc. Roy. Soc.*, **42** (1887), 111—131).

spectrum of the same earth it has no action. Is the basis of this earth simple or compound?

5. An earth* showing no difference on fractionation has a phosphorescent spectrum not materially modified by the admixture of another earth; but the residual glow of one part of the spectrum as seen in the phosphoroscope is suppressed, while that of the other is not affected. Are we not here also dealing with more than one sort of molecule?

6. Earths,† apparently the same, from different minerals, behave alike chemically and spectroscopically, with the exception that a certain line in the spectrum of the one is a little brighter than the corresponding line in the spectrum of the other.

Again, where are we to draw the line? If an immediate decision were required, and a poll of the chemists in this room demanded, we should probably find the dividing lines placed in all positions among these seven cases.

But to have only one rank in the elementary hierarchy, to class these obscure and indefinite bodies in the same rank with silver and chlorine and oxygen and sulphur, is as manifest an absurdity as it would be to put a speck of meteoric dust upon a level with the planet Jupiter because both may be called distinct members of the solar system.

Is there no way out of this perplexity? Must we either make the elementary examination so stiff that only some 60 or 70 candidates can pass, or must we open the examination doors so wide that the number of admissions is limited only by the number of applicants?

The real difficulty we encounter by unlimited multiplication of elements arises from the Periodic theory. That theory has received such abundant verification that we cannot lightly accept any interpretation of phenomena which fails to be in accordance with it. But if we suppose the elements reinforced by a vast number of bodies slightly differing from each other in their properties, and forming, if I may use the expression, aggregations of nebulæ where we formerly saw, or believed we saw, separate stars, the periodic arrangement can no longer be definitely grasped. No longer, that is, if we retain our usual conception of an element. Let us then modify this conception. For "element" read "elementary group," such elementary groups taking the place of the old elements in the periodic scheme,—and the difficulty falls away.

* Calcium sulphate and many other bodies behave in this manner in the phosphoroscope (*Proc. Roy. Soc.*, **42** (1887), 120).

† Yttrium from different minerals shows great variations of intensities in all its lines. Gζ appears in greater quantity in samarskite than it does in gadolinite (*Chem. News*, **54** (1886), 157).

In defining an element, let us not take an external boundary, but an internal type. Let us say, *e.g.*, the smallest ponderable quantity of yttrium is an assemblage of ultimate atoms almost infinitely more like each other than they are to the atoms of any other approximating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium, therefore, merely represents a mean value around which the actual weights of the individual atoms of the "element" range within certain limits. But if my conjecture is tenable, could we separate atom from atom, we should find them varying within narrow limits on each side of the mean.

The very process of fractionation implies the existence of such differences in certain bodies. Until lately such bodies passed muster as elements. They had definite properties, chemical and physical; they had recognised atomic weights. If we take a pure dilute solution of such a body, yttrium for instance, and if we add to it an excess of strong ammonia, we obtain a precipitate which appears perfectly homogeneous. But if instead we add very dilute ammonia in quantity sufficient only to precipitate one half of the base present, we obtain no immediate precipitate. If we stir up the whole thoroughly so as to ensure a uniform mixture of the solution and the ammonia, and set the vessel aside for an hour, carefully excluding dust, we may still find the liquid clear and bright without any vestige of turbidity. After three or four hours, however, an opalescence will declare itself, and the next morning a precipitate will have appeared.

Now, let us ask ourselves what can be the meaning of this phenomenon?

The quantity of precipitant added was insufficient to throw down more than half the yttria present, therefore a process akin to selection has been going on for several hours. The precipitation has evidently not been effected at random, those molecules of the base being decomposed which happened to come in contact with a corresponding molecule of ammonia, for we have taken care that the liquids should be uniformly mixed, so that one molecule of the original salt would not be more exposed to decomposition than any other. If, further, we consider the time which elapses before the appearance of a precipitate, we cannot avoid coming to the conclusion that the action which has been going on for the first few hours is of a *selective* character. The problem is not *why* a precipitate is produced, but *what determines* or directs some atoms to fall down and others to remain in solution. Out of the multitude of atoms present, what power is it that directs each atom to choose the proper path? We may picture to ourselves some directive force passing the atoms one by one in review, selecting one for precipitation and another for solution, till all have been adjusted.

In order that such a selection can be effected there evidently must be some slight differences between which it is possible to select, and this difference almost certainly must be one of basicity, so slight as to be imperceptible by any test at present known, but susceptible of being nursed and encouraged to a point when the difference can be appreciated by ordinary tests.

Fig. 1.

Let us follow our atoms through another stage of fractionation. The ammonia has divided them into two groups, one of which displays just the minutest possible suspicion of greater basicity than the other. Let us repeat the first experiment again with these two groups. Again, we obtain from each a precipitate and a solution, so that we have now two precipitates and two solutions. It is evident that whereas the precipitate from the original salt was slightly less basic than that which remained dissolved, the second precipitate from the first precipitate must have its basic character still further diminished, while at the same time the second solution from the first solution must contain selected atoms of a slightly higher degree of basicity. The least basic at one end and the most basic at the other end are thus two removes each from the original; and treating them in the same way for a third time, we obtain two groups of atoms which are three removes from the centre. (The intermediate groups need not be here

discussed. By systematic mixings they can be made to contribute their quota to the end groups.) By repeating this operation, not once or twice but many hundreds of times, those atoms having a tendency to come down first always going one way, and those having a tendency to remain dissolved always going the other way, we, so to speak, *educate* the atoms, adding to them no fresh properties, but drawing out and giving free scope to properties that already existed, but that were previously masked.

A similar absence of absolute homogeneity may possibly yet be traced in many of the "elements" if once the right reagents are selected, and if laborious chemists are to be found willing to devote years to researches barren to outward seeming.

That this deviation from absolute homogeneity should mark the constitution of these molecules* or aggregations of matter which we designate elements will perhaps be clearer if we return in imagination to the earliest dawn of our material universe, and, face to face with the great secret, try to consider the processes of elemental evolution.

Going back to the "fire-mist," the "ur-stoff" of the German philosophers, or the "protyle," as, after Roger Bacon, I have ventured to call it, we see an infinite number of immeasurably small ultimate, or rather ultimatissimate particles gradually accreting out of "formless stuff," and moving with inconceivable velocity in all directions. We find those particles which approximately have the same rate and modes of movement, beginning to heap themselves together by virtue of that ill-understood tendency through which like and like come together—that principle by virtue of which identical or approximately identical bodies are found collected in masses in the earth's crust instead of being uniformly distributed.

One of the first results of this massing tendency is the formation of certain nodal points in space, between which occur approximately void intervals. How such nodes and spaces come to be formed we shall be better able to understand by a very few simple illustrations, choosing in the first instance, instead of ultimate atoms, living men and women.

If we take any very frequented street in London, say Fleet Street, at a time when the animated current runs pretty equally in two directions, and if our rate of walking is somewhat greater than the mean speed of the other foot passengers, we shall observe that the throngs on the footways are not evenly distributed, but consist of knots or groups—we might almost say blocks—with comparatively open intervening spaces. The explanation of this unequal agglomeration of

* Clerk-Maxwell defines a molecule as "a material system, the parts of which are connected in some definite way." ("Atom," *Encyclopædia Britannica*, 9th Ed., 3, 43.)

individuals is simple. Some two or three persons whose rate of walking is slower than the average somewhat retard the movements of other persons, whether travelling in the same or in the opposite direction. In this manner a slight temporary obstruction is created. The persons behind catch up to the obstruction, and so increase it, while those in front of the obstruction, hurrying on unhindered at their former rate, leave a comparatively free and open space, until they, too, find themselves delayed further on by another little group of loiterers.

The same process may be observed with vehicles in the carriage-way of much frequented streets. Thus we find that differences in rate of movement are sufficient to arrange a multitude of moving bodies into a series of knots and gaps.

In a crowded thoroughfare like Fleet Street, with two opposing human currents, much regularity in the sequence of these knots and voids is not to be expected; but if the observer happens to be walking with a crowd whose constituents are travelling in the same direction, the regularity becomes more apparent; and if, as is sometimes the case, a little rhythm is infused into the steps by an accompaniment of music, the knots and gaps become so orderly that the distance between one block and another, measured in yards, will be found not to differ very greatly from one end of the road to the other.

If, instead of men and women, we experiment with little grains of substances of approximately equal size, but differing in specific gravity, and, mixing them in a horizontal tube with water, we set them in movement by rhythmical agitation, similar phenomena will occur, and the heavy and light powders will sort themselves in a very regular manner.* Descending to a lower degree of minuteness, we all know what occurs when an induction current is passed through a rarefied gas. Here the particles, being exempt from free will or caprice, implicitly obey the law I have attempted to illustrate, and out of infinite disorder, under the influence of the electric rhythm, sort themselves into beautiful forms of stratifications.

Let us now return to our ultimate atoms, where the case, though much more complicated, is of the same character. We will suppose certain points in space where the first step in differentiation has been achieved. The ultimate particles have commenced to vibrate in their

* "The atoms run like to like, as you may see either in the case of seeds which are being winnowed in a sieve, or in the case of pebbles on the sea shore; for on account of the whirling of the sieve beans are separated and go with beans, barley with barley, and wheat with wheat; and on account of the motion of the waves, the longish pebbles are driven to the same spot as the longish ones, and the round with the round."—Democritus, in a fragment given in *Sextus Math.* (vii, 116 seq.). "The Atomic Theory of Lucretius," by John Masson. 1884, p. 66.

new born energy in all directions, and with velocities ranging from zero to infinity.* The law which we have traced from animated beings and coarse powders, down to the molecules of a rarefied gas, still holds good at this transcendental stage of matter, and the imagination can picture knots and voids gradually forming there as well as in Fleet Street. The slower particles will obstruct the quicker, the more rapid will rush up to the laggards in front, and we shall soon have groups forming in different parts of space. The constituents of each group whose rate of vibration is not in accord with the mean rate of the bulk of the components of that group will work to the outside and be thrown off to find other groups with which they are more in harmony. In time, therefore, a condition of stability is established between the various groups, and we may call these the molecules of our present system of elementary bodies.

With regard to the place where atoms come into existence, it seems to me almost certain that if their existence has had a beginning, it has begun at the very edge of the protyle, or the confines of the ponderable Universe, and that their subsequent migrations have always been inwards.

In dynamical language, every new position into which an atom can glide must be from a position of higher to a position of lower potential. If the atom has had a beginning it must therefore have been where the potential is highest, *i.e.*, on the confines of the ponderable Universe, and if it comes to an end it must be where the potential is lowest, *i.e.*, in the centre of overgrown stars; so that the extinction of the central part of a star when it becomes overgrown is that which puts a limit to the size a star can attain by attracting to itself surrounding matter. This assigning of the places where chemical atoms have their origin and where they meet with extinction seems the only—or almost the only—conclusion we can yet with confidence advance.†

* Maxwell, "Atom," *Encyclopædia Britannica* (9th Ed.), 3, 40.

† For this fruitful suggestion and for other valuable criticism and advice on parts of this address I am indebted to my friend G. Johnstone Stoney, M.A., F.R.S.

Mr. G. Johnstone Stoney has given in the *Times* of April 4th, the following explanation of this passage:—

"There is nothing more certain in physical science than that, if atoms of ponderable matter are generated by any process of nature, they will inevitably thenceforth gravitate inwards towards the rest of the ponderable matter of the universe, and that, therefore, they must have come into existence at a position further out than those through which they subsequently pass. It may further be stated that some at least must have been formed at or beyond the limits now occupied by any ponderable matter. And it is also certain that their extinction, if it arrives at all, must overtake them in the position of lowest potential which they can reach, and that the position of lowest potential is at the centre of the largest star.

"You regard a limit to the universe as having been gratuitously invented for this

From the above illustrations it will be seen that the constituent atoms of these molecules originally may not have been gifted with exactly the same speed or amplitude of vibration. In the molecule of a certain group let the form of energy which has for a factor what we call atomic weight be represented by the figure 35·5; it follows, from the foregoing exposition—which I have endeavoured to make clear—that whilst the great bulk of its component atoms have this

theory. But have you not here overlooked what we are taught by the other sciences which, along with chemistry, bring us our knowledge of Nature? The lesson to which astronomy points is that the universe is limited. We know that the stars which constitute our Milky Way, our sun, and all the stars we see of a clear night form a detached group. It is certainly possible, and the facts that are known about the nebula in Andromeda make it probable that there exist other groups of stars as numerous as we see in the Milky Way and scattered over our sky. The spectroscope indicates that that great nebula consists of stars, although their great distance precludes their being seen separately by any telescope, and their aggregate brightness is about the same as that of the Milky Way; in other words, they present very much the appearance which our great group of stars would have if seen from an equal distance. Moreover, a star outburst appeared among them, as has from time to time happened in our part of the universe. From these facts we may with probability infer that this nebula is a group of stars comparable to our great group. But that there are not an infinite number of such groups seems almost certain. It is a familiar theorem in optics that if stars in unlimited numbers sent us their radiations we should have 200,000 times as much light and heat as we actually receive, unless the radiations are absorbed or intercepted on the way to such an extent that only one two-hundred-thousandth part reaches us. This is so improbable that the alternative conclusion, that the universe is limited, is with some emphasis declared by astronomy. It was not, therefore, invented for the exigencies of the chemical hypothesis. Nor is a limited universe necessary for the statement made by Mr. Crookes. Whether limited or not, the ponderable universe consists of detached stellar groups, that of our Milky Way, that of the great nebula in Andromeda, and perhaps some others. The vast celestial spaces between these groups are beyond the confines of the universe in the sense required by Mr. Crookes's statement,—they are outside the universe of ponderable matter.

"Astronomy again comes to our aid with reference to the locality where atoms may become extinguished. Stars are not of all sizes. There is a distinct limit beyond which they cannot be ascertained to grow. The variety of their dimensions is like that found among the pebbles of a gravelled walk. There are none among them which, in comparison, are mountain masses or even boulders. There is, therefore, some cause in nature which puts this limit to their growth. And if chemical elements anywhere meet with extinction, this limitation of the size of stars is fully accounted for. On dynamical principles the extinction of an atom can only occur when it reaches its position of lowest potential, and the position of lowest potential is at the centre of the greatest star.

"It has always appeared to my mind a great recommendation of the hypothesis that there are processes in nature which convert radiant energy into the energy stored up in ponderable matter, that it relieves us from the vastly greater improbability of the only alternative hypothesis, viz., that the entire universe will become motionless and inert through the equable distribution or complete dissipation of its energy."

atomic weight, a small percentage may vary from this figure to the extent of a decimal place, while a few others may stray as much as a whole number or two on one side or the other of the mean. The ultimate atoms whose rates are not exactly 35·5, but a little higher or lower than 35·5, will congregate around the 35·5 nucleus, forming a group whose average value will be 35·5. In like manner similar groups will be formed having the average rates of 80 and 127, whilst intermediate spaces will be cleared, the ultimate atoms which occupied these lone spaces being attracted to the chlorine, bromine, and iodine groupings. These groupings represent what at present we call elements, but which I conjecture may possibly consist each of an element and of a certain number of meta-elements, or each may be formed of a whole group of meta-elements, none of which greatly preponderates over the remainder.

On the threshold we encounter an objection very clearly stated by Clerk-Maxwell in his *Theory of Heat* (1871). "I do not think," says this eminent physicist, "that the perfect identity which we observe between different portions of the same kind of matter can be explained on the statistical principle of the stability of the averages of large numbers of quantities each of which may differ from the mean; for if of the molecules of some substance, such as hydrogen, some were of slightly greater mass than others, we have the means of producing a separation between molecules of different masses, and in this way we should be able to produce two kinds of hydrogen, one of which would be somewhat denser than the other. As this cannot be done, we must admit that the quality which we assert to exist between the molecules of hydrogen applies to each individual molecule, and not merely to the average of groups of millions of molecules."

"The molecules of the same substance are all exactly alike, but different from those of other substances. There is not a regular gradation in the mass of molecules from that of hydrogen, which is the least of those known to us, to that of bismuth; but they all fall into a limited number of classes or species, the individuals of each species being exactly similar to each other, and no intermediate links are found to connect one species with another by a uniform gradation."

"In the case of molecules, however, each individual is permanent; there is no generation or destruction, and no variation, or rather no difference, between the individuals of each species."

"Our molecules are unalterable by any of the processes which go on in the present state of things, and every individual of each species is of exactly the same magnitude, as though they had all been cast in the same mould like bullets, and not merely selected and grouped according to their size, like small shot."

I think it evident that the statements here quoted, some of which involve no small amount of assumption, no longer accord with facts, for we actually do find variations between the properties of certain molecules which heretofore had been pronounced identical with each other. Take the case of yttrium. It had its definite atomic weight; it behaved in every respect as a simple body, an element, to which we might indeed add, but from which we can not take away. Yet this yttrium, this supposed homogeneous whole, on being submitted to a certain method of fractionation is resolved into portions not absolutely identical among themselves, and exhibiting a gradation of properties.

Or take the case of didymium: here was a body betraying all the recognised characters of an element. It had been separated with much difficulty from other bodies which approximated closely to it in their properties, and during this crucial process it had undergone very severe treatment and very close scrutiny. In short, until lately we might have said of it just what Clerk-Maxwell says of hydrogen, that the equality which we assert to exist between the molecules of didymium applies to each individual molecule, and not merely to the average of groups of millions of molecules. But then came another chemist, who, treating this assumed homogeneous body by a peculiar process of fractionation, resolved it into the two bodies praseodymium and neodymium, between which certain distinctions are perceptible. Further, we even now have no certainty that neodymium and praseodymium are simple bodies. On the contrary, they likewise exhibit symptoms of splitting up.

Now if one supposed element on proper treatment is thus found to comprise dissimilar molecules, we are surely warranted in asking whether similar results might not be obtained in other elements, perhaps in all elements, if treated in the right way? We may even ask where the process of sorting-out is to stop? a process which of course presupposes variations between the individual molecules of each species.

And in these successive separations we naturally find bodies approaching more and more closely to each other. Dr. Auer von Welsbach, the discoverer of neodymium and praseodymium, remarks that these bodies "approximate more closely to each other than any two supposed simple bodies yet known." Thus we approach nearer and nearer either to a regular gradation in the molecules or to the recognition of those intermediate links, which I have named "meta-elements" or elementoids. A suggestion here occurs that it may be to the presence of these meta-elements that so many of the chemical elements, whilst approching closely in their atomic weights the values required by Prout's law, deviate from it by a small but measurable

amount. We can scarcely regard their approximation as purely accidental.

We now come to the last objection pertinently put forth by Clerk-Maxwell to the hypothesis that the elements are not absolutely homogeneous. He writes:—"It is difficult to conceive of selection and elimination of intermediate varieties, for where can these eliminated molecules have gone to if, as we have reason to believe, the hydrogen, &c., of the fixed stars is composed of molecules identical in all respects with our own?"

In the first place we may call in question this absolute molecular identity, since we have hitherto had no means for coming to a conclusion save the means furnished by the spectroscope, whilst it is admitted that for accurately comparing and discriminating the spectra of two bodies they should be examined under identical states of temperature, pressure, and all other physical conditions. We have certainly seen, in the spectrum of the sun, rays which we have not been able to identify.

We have supposed the cosmic cycle re-entering in successive periods, during a fall of temperature, the same region—say, for instance, where chlorine, bromine, or iodine have been formed. If most of the atoms present approximate more or less closely to 35·5, 80, or 127—the atomic weights of these three bodies—they will be in consequence easily disposed of. But there may be besides a few intermediate atoms having, say atomic weights of between 36 and 79 and between 81 and 126. These atoms will be attracted to the masses on one side or the other of the cyclical track. We can even imagine sparse atoms scattered so far from the centre line of track as to be midway between chlorine and bromine or between bromine and iodine; these wanderers likewise will be slowly picked up and will gravitate to chlorine, bromine, or iodine; and, being thus accounted for, none need be eliminated.

It is not impossible, moreover, that the elementary atoms themselves are not the same now as when first generated. For if an atom has commenced its existence at a certain epoch, and may go through such vicissitudes that it will cease to exist, it seems at least probable that it may undergo inward change. These vicissitudes probably directly affect only the primary motions which constitute the existence of the atom, but they indirectly, and only in a slight degree, affect those secondary motions which produce all the effects we can observe—chemical effects, heat effects, electrical, and so on. Thus, while the life of an atom may be waning away under the various experiences to which it is subjected, it may, and probably does, appear to us the same as at first. But perhaps not quite, so that atoms originally alike, taken from different minerals collected at widely

separated stations on the earth, *may* have had sufficiently different past histories to have come to be markedly different in regard to the primary motions which elude our observation, and through the very slight influence which changes in the primary motions have on the secondary motions, *may* be just perceptibly different under our experiments. From this point of view a rare element, like a rare plant or animal, is one which has failed to develop in harmony with its surroundings.

This view lends itself very naturally to the facts we encounter in our fractionation experiments. Where all the ultimate atoms have precisely identical rates of vibration, any fractionation is impossible. Where such rates are not identical the process proves successful; and all the more easily the wider the differences among the vibration-rates of the ultimate atoms. The bodies thus split off necessarily very closely approximate to each other, and the further we push our fractionations the less marked are the differences.

But as we review the series of elements arranged on the curve I adopted from Professor Emerson Reynolds to illustrate my address on the "Genesis of the Elements" delivered before the Chemical Section of the British Association (Birmingham Meeting), we cannot fail to be struck by a consideration which at first sight appears absolutely fatal to the notion of the production of the elements from a series of "knots," as just described. If the element which we call aluminium has been formed from ultimate atoms having rates of vibration of the rate 27, or a little more or less so as to give a mean of 27, and if the atoms between aluminium and the next element in the series have in this manner been sorted out to the one hand or the other, leaving a void between, we should expect that their properties would not differ very widely from each other, or at least that they would present considerable analogies. Now to a certain extent this is actually the case. Upon aluminium follows silicon. We may perhaps conceive these two elements as springing from the differentiation of a nearly homogeneous swarm of ultimate atoms. But if we pursue the curve onwards, what elements follow? Phosphorus, sulphur, and chlorine, bodies heterologous with each other and heterologous with silicon. We can scarcely imagine original atoms, so to speak, in doubt which of two aggregations they should join, the one being silicon and the other phosphorus. Nor can we conceive of anything being split off from sulphur which should make even the slightest approximation to chlorine.

It appears to me, however, that these difficulties are more apparent than real. In the Birmingham Address already referred to, I asked my audience to picture the action of two forces on the original protyle, one being *time*, accompanied by a lowering of temperature;

the other, swinging to and fro like a mighty pendulum, having periodic cycles of ebb and swell, rest and activity, being intimately connected with the imponderable matter, essence, or source of energy we call *electricity*. Now a simile like this effects its object if it fixes in the mind the particular fact it is intended to emphasize, but it must not be expected necessarily to run parallel with all the facts. Besides the ebb and flow of temperature with the periodic ebb and flow of electricity, positive or negative, requisite to confer on the newly born elements their particular atomicity, it is evident that a third factor must be taken into account. Nature does not act on a flat plane; she demands space for her cosmogenic operations, and if we introduce *space* as the third factor all appears clear.

Instead of a pendulum, which though to a certain extent a good illustration is impossible as a fact, let us seek some more satisfactory way of representing what I conceive may have taken place. Let us suppose the zigzag diagram not drawn upon a plane, but projected in space of three dimensions. What figure can we best select to meet all the conditions involved?

Many of the facts can be well explained by supposing the projection in space of Professor Emerson Reynolds's zigzag curve to be a spiral. This figure is, however, inadmissible, inasmuch as the curve has to pass through a point neutral as to electricity and chemical energy twice in each cycle. We must therefore adopt some other figure. A figure of eight or lemniscate will foreshorten into a zigzag just as well as a spiral, and it fulfils every condition of the problem. Such a figure will result from three very simple simultaneous motions. First a simple oscillation backwards and forwards (suppose east and west); secondly, a simple oscillation at right angles to the former (suppose north and south), of half the periodic time, *i.e.*, twice as fast; and thirdly, a motion at right angles to these two (suppose downwards), which, in its simplest form, would be with unvarying velocity.*

If we project this figure in space we find on examination that the points of the curves where chlorine, bromine, and iodine are formed come close under each other; so also will sulphur, selenium, and tellurium; again, phosphorus, arsenic, and antimony, and in like manner other series of analogous bodies.

It may be asked whether this scheme explains *how* and *why* the elements appear in this order? Let us imagine a cyclical translation in space, each revolution witnessing the genesis of the group of elements which I previously represented as produced during one complete vibration of the pendulum. Let us suppose that one cycle

* Put into their simplest mathematical dress, the first of these motions is represented by $x = a. \sin(mt)$, the second by $y = b. \sin(2mt)$, and the third by $z = c. t.$

has thus been completed, the centre of the unknown creative force in its mighty journey through space having scattered along its track the primitive atoms, the seeds, if I may use the expression, which presently are to coalesce and develop into the groupings now known as lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine.

What is most probably the form of track now pursued? Were it strictly confined to the same plane of temperature and time, the next elementary groupings to appear would again have been those of lithium, and the original cycle would have been eternally repeated, producing again and again the same fourteen elements. The conditions, however, are not quite the same. Space and electricity are as at first; but temperature has altered, and thus, instead of the atoms of lithium being supplemented with atoms in all respects analogous with themselves, the atomic groupings which come into being when the second cycle commences form not lithium but its lineal descendant potassium.

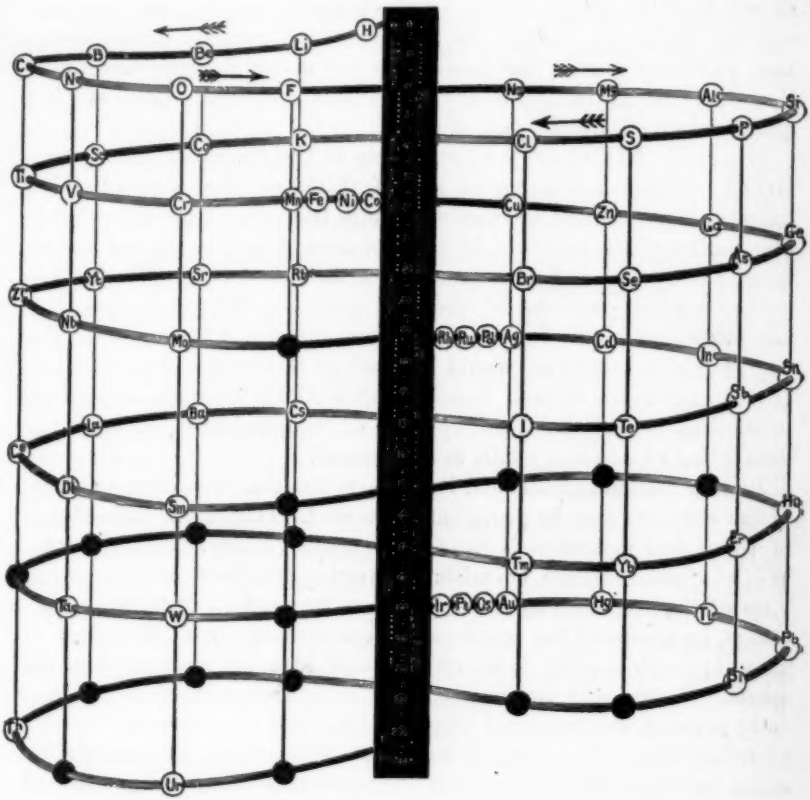
Suppose, therefore, the *vis generatrix* travelling to and fro in cycles along a lemniscate path as above suggested, while simultaneously temperature is declining and time is flowing on (variations which I have endeavoured to represent by the downward sink); each coil of the lemniscate track crosses the same vertical line at lower and lower points. Projected in space, the curve shows a central line neutral as far as electricity is concerned and neutral in chemical properties—positive electricity on the north, negative on the south. Dominant atomicities are governed by the distance east and west from the neutral centre line, monatomic elements being one remove it, diatomic two removes, and so on.*

In every successive coil the same law holds good. As the mighty focus of creative energy goes round we see it in successive cycles sowing in one tract of space seeds of lithium, potassium, rubidium, and cæsium; in another tract, chlorine, bromine, and iodine; in a third, sodium, copper, silver, and gold; in a fourth, sulphur, selenium, and tellurium; in a fifth, beryllium, calcium, strontium, and barium;

* In the model curve, Fig. 2, the elements are supposed to follow one another at equal distances along the lemniscate spiral. The vertical scale is divided into 240 equal parts, on which the atomic weights are plotted, from H = 1 to Ur = 239. Each ball representing an element is accurately on a level with its atomic weight on the vertical scale. Metallic elements are silvered; it will be seen that with one or two exceptions all the metals are on the north side. Missing elements are represented black. A few doubtful elements:—didymium, samarium, erbium, holmium, and thulium,—are inserted in the positions required by the atomic weights usually assigned to them; a glance, however, will show that they have no right to the places they occupy.

in a sixth, magnesium, zinc, cadmium, and mercury; in a seventh, phosphorus, arsenic, antimony, and bismuth; in other tracts, alum-

FIG. 2.



inium, gallium, indium, and thallium; silicon, germanium, and tin; carbon, titanium, and zirconium; whilst a natural position near the neutral axis is found for the three groups of elements relegated by Professor Mendeléeff to a sort of hospital for incurables—his 8th family.

We have now traced the formation of the chemical elements from knots and voids in a primitive, formless fluid. We have shown the possibility, nay, the probability, that the atoms are not eternal in existence, but share with all other created beings the attributes of decay and death. We have shown, from arguments drawn from the chemical laboratory, that in matter which has responded to every test of an element, there are minute shades of difference which may

admit of selection. We have seen that the time-honoured distinction between elements and compounds no longer keeps pace with the developments of chemical science, but must be modified to include a vast array of intermediate bodies—" meta-elements." We have shown how the objections of Clerk-Maxwell, weighty as they are, may be met; and, finally, we have adduced reasons for believing that primitive matter was formed by the act of a generative force, throwing off at intervals of time atoms endowed with varying quantities of primitive forms of energy.

If we may hazard any conjectures as to the source of energy embodied in a chemical atom, we may, I think, premise that the heat radiations propagated outwards through the ether from the ponderable matter of the universe, by some process of nature not yet known to us, are transformed at the confines of the universe into the primary —the essential—motions of chemical atoms, which the instant they are formed gravitate inwards, and thus restore to the universe the energy which otherwise would be lost to it through radiant heat. If this conjecture be well founded, Sir William Thomson's startling prediction of the final decrepitude of the universe through the dissipation of its energy falls to the ground.

In this fashion, gentlemen, it seems to me that the great question of the elements may be provisionally treated. Our slender knowledge of these first mysteries is extending steadily, surely, though slowly. Whilst certain ardent chemists are testing the commonly received view of the homogeneity of the elements by methods of fractionation, others, by means of the spectroscope, are carrying on another form of assault; each worker bent on the one idea of undermining the secret. I earnestly recommend such researches. However successfully pursued, they cannot, I know, lead directly to any results capable of being turned to industrial account. If, however, we consider the small but firm foothold we have gained in pursuit of this line of investigation, I venture to think there is reasonable ground to hope that these researches may tend to place chemistry upon a new foundation, by penetrating down through loose, superficial matter to the solid rock.

The application of the luminous principle of evolution has remodelled and vivified many branches of biology; and philosophers are eagerly invoking its aid in other departments of science; I would fain hope that I may not be deemed unduly sanguine in believing that the application of this regenerating principle to chemistry will produce far-reaching effects on its harmonious and progressive development.

Dr. Gladstone then moved that thanks be given to the President

for his address, and that he be requested to allow it to be printed. The motion was seconded by Dr. Atkinson, and carried with acclamation. The President having replied, the Treasurer, Dr. Russell, gave an account of the financial condition of the Society. The receipts by admission fees and subscriptions had been £3158; by sale of Journal, £351 11*s.* 1*d.*; by dividends on invested capital, £317 12*s.* 9*d.*; the whole income being £3896 2*s.* 10*d.* The expenses on account of the Journal had been £2116 10*s.* 4*d.*; on account of the Abstracts of Proceedings, £140 15*s.* 5*d.*; on account of the Library, £365 7*s.* 10*d.*; the total expenditure being £3194 1*s.* 4*d.* £300 had been invested in Metropolitan Board of Works 3½ per cent. stock, and there was a balance in hand of £1672 19*s.* 3*d.*

Dr. T. Stevenson moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Mr. J. A. R. Newlands seconded the motion. Dr. Russell acknowledged the vote.

A vote of thanks to the auditors was proposed by Professor Ramsay, seconded by Mr. Friswell, and acknowledged by Professor Dunstan.

Mr. Heaton proposed a vote of thanks to the Officers and Council; the vote was seconded by Professor Dunstan, and acknowledged by Dr. Armstrong.

Professor Clowes moved that the thanks of the Society be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. Plimpton seconded the motion. Mr. Groves and Dr. Thorne replied.

Messrs. Heron and Jackson having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: W. Crookes, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; Warren de la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; David Howard; J. W. Mallet, M.D., F.R.S.; H. McLeod, F.R.S.; Ludwig Mond; C. Schorlemmer, Ph.D., F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, M.A., Ph.D., F.R.S.

Treasurer: W. J. Russell, Ph.D., F.R.S.

University of Michigan

Dr. The Treasurer in Account with the Chemical Society from March 21, 1887, till March 21, 1888. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 21st, 1887	1,297	3	0			
,, in hands of Treasurer	4	7	3			
				1,301	10	3
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 21st, 1887, to March 21st, 1888.						
25 Life Compositions	500	0	0			
110 Admission Fees	440	0	0			
3 Subscriptions for 1884	5	0	0			
20 ,, ,, 1885	38	0	0			
78 ,, ,, 1886	141	0	0			
321 ,, ,, 1887	634	0	0			
715 ,, ,, 1888	1,398	0	0			
1 ,, ,, 1889	2	0	0			
				3,158	0	0
Sale of Journal and Index				351	11	1
Subscriptions for Proceedings of Royal Society				38	0	0
,, from Institute of Chemistry				6	5	0
,, from Society of Public Analysts				4	4	0
,, ,, ,, Chemical Industry (for 5 years)				21	0	0
Dividends on Consols				116	10	0
,, Metropolitan Board of Works 3½ per Cent. Stock				170	11	6
,, London and North Western Railway Debenture Stock				30	11	3
				5,198	3	1

Assets.	£	s.	d.
Balance at Bank	1,672	12	0
,, in hands of Treasurer	0	7	3
Three per Cent. Consols	4,000	0	0
London and North Western Railway Debenture Stock	788	0	0
Metropolitan Board of Works 3½ per cent. Stock	5,100	0	0

Expenses on Account of the Journal.	£	s.	d.	£	s.	d.
Salary of the Editor	250	0	0			
Salary of the Sub-Editor	100	0	0			
Miscellaneous Expenses of Editors	3	0	0			
Fees to Abstractors	261	8	6			
Printing of Journal	1,240	8	2			
Distribution of Journal	261	13	8			
				2,116	10	4
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	197	5	9			
Binding, Catalogue Cards, Boxes for Periodicals	56	2	1			
				365	7	10
Printing Authors' Copies				46	7	6
Proceedings of Royal Society				60	0	0
Distribution of Proceedings of Royal Society				3	15	7
Printing and Distribution of Abstracts of Proceedings				140	15	5
Miscellaneous Printing				29	19	6
Post Card Account				1	15	6
Inhabited House Duty and Income-tax				9	5	0
Stationery				31	13	4
Furniture and Repairs				29	19	5
Collector's Commission on Subscriptions				157	12	0
Treasurer's Stamps and Drafts				5	14	8
Jubilee Expenses: Address to Queen (£5), Decoration of Piccadilly Fund (£10)				15	0	0
House Expenses.						
Providing Refreshments	18	0	2			
Heating the Building	18	10	0			
Lighting ,,	52	13	9			
Cleaning ,,	20	0	0			
Petty House Expenses	7	10	5			
Wages of House Porter	59	12	6			
				176	6	10
Treasurer's Petty Cash Disbursements				3	18	5
Purchase of £300 Metropolitan Board of Works 3½ per cent. Stock				331	2	6
Balance at Bank	1,672	12	0			
,, in hands of Treasurer	0	7	3			
				1,672	19	3
				5,198	3	1

Audited with vouchers and found correct. { Wyndham R. Dunstan. C. W. Heaton. Samuel Rideal.

March 24th, 1888.

Treasurer of the Chemical Society in Account with Research Fund.

From March 21st, 1887, till March 21st, 1888.

Dr.

1887.		£	s.	d.
Mar. 21.	Balance at Bank	237	5	6
Aug. 9.	Subscription from Drapers' Company	105	0	0
	Dividends on Metropolitan Board of Works 3½ per cent. Stock	134	1	6
	Dividend on North British Railway Stock	38	14	5
		£515	1	5

Assets.	£	s.	d.
North British Railway 4 per cent. Stock	1,000	0	0
Metropolitan Board of Works 3½ per cent. Stock	4,000	0	0
Balance at Bank	309	11	5
	£5,309	11	5

Cr.

	£	s.	d.
Grants made	95	0	0
Purchase of £100 Stock in Metropolitan Board of Works Stock	110	10	0
Balance at Bank	309	11	5
	£515	1	5

Audited with vouchers and found to be correct,
March 24th, 1888.

Wyndham R. Dunstan.
C. W. Heaton.
Samuel Rideal.

Ordinary Members of Council: Messrs. T. Carnelley, D.Sc.; A. H. Church; Frank Clowes, D.Sc.; Wyndham Dunstan; P. F. Frankland, Ph.D.; R. J. Friswell; Charles W. Heaton; E. Kinch; H. F. Morley, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.; W. Ramsay, Ph.D.

OBITUARY NOTICES.

CHARLES LOUDON BLOXAM was born on the 23rd March, 1831, at Meriden, Warwickshire, where his father had a medical practice. Dr. Bloxam subsequently came to London, and in 1842 his son Charles was sent to King's College School.

Charles Bloxam remained there for two years, and in 1845 he was entered as one of the earliest students at the Royal College of Chemistry under Professor Hofmann. His progress under that teacher was very rapid, and in 1849 he was appointed Assistant at the College.

After occupying this post for a year he resigned and obtained a considerable private practice as an analyst and teacher at his laboratory in Duke Street, Grosvenor Square. During this time in conjunction with Mr., now Sir Frederick, Abel he wrote the *Handbook of Chemistry* which was first published in their joint names in the year 1853.

Professor Bloxam's forte, however, lay in his power as a teacher, and feeling this he became a candidate for the post of Demonstrator of Chemistry in King's College, London, when a vacancy occurred in 1854. At that time the Chair was divided, Dr. William Allen Miller being Professor of Theoretical Chemistry, and Mr. John Bowman of Practical Chemistry. On the death of the latter in 1856, Mr. Bloxam was appointed to conduct the classes in Practical Chemistry, and in 1870 on the death of Dr. Miller the Council combined the two chairs, appointing Professor Bloxam as the sole occupant.

Besides the different posts which Professor Bloxam held in connection with King's College, he was also connected with the Royal Military Academy and the Royal Artillery College, Woolwich. He succeeded Sir F. Abel as Lecturer on Chemistry at the former establishment in 1855, and afterwards held the joint Lecturership of Chemistry and Physics until 1882, and the Lecturership on Chemistry at the Artillery College from 1864 until his death.

Professor Bloxam was beyond doubt one of the most successful teachers in experimental science of his time. The great pains which

he took in the direction of making his lectures explicit and interesting both by clear reasoning and good experimental illustration left him little time for original research.

Although he gave 13 lectures a week for nine months of the year for nearly 20 years, he almost invariably wrote fresh lecture notes for each course, ever attempting to consider the matter in some clearer light, and to impart fresh interest to the subjects of his lectures, by new experimental illustrations.

His text-book, *Chemistry, Inorganic and Organic*, was first published in 1866, and the sixth edition had just gone through the press when he died. His *Laboratory Teaching* first appeared in 1869, and Professor Bowman's *Practical Chemistry* has also been edited through the last six editions.

Professor Bloxam was elected a Fellow of the Chemical Society in 1854, and has contributed various papers to the Society, chiefly on Mineral and Analytical Chemistry, besides publishing numerous smaller communications in the *Chemical News*.

Unfortunately, the state of his health prevented him from appearing in the world outside King's College and his lecture rooms at Woolwich. He suffered of late years from extreme delicacy of the lungs, which obliged him to exercise great care, and it was to this disease that he ultimately succumbed on the 28th November, 1887, at the comparatively early age of 56.

Jean Baptiste Joseph Dieudonné Boussingault was born in Paris on February 2nd, 1802. He received his scientific education at the School of Mines of St. Étienne; and in the laboratory of that institution he conducted his first investigation—on silicides of platinum—the results of which were published in 1821. Shortly afterwards he was appointed to a Professorship in the School of Mines of Bogotá, in Colombia, South America. But the South American War of Independence broke out soon after his arrival, and Boussingault attached himself to Bolivar, the leader of the insurrection, whose aide-de-camp he became. After the war, he accepted the post of manager of some mines for an English company in Colombia. He remained there for about ten years, and during that period found time to publish some 50 scientific memoirs, chiefly on metallurgical or mineralogical subjects. But before leaving Europe he had received valuable suggestions as to the points deserving observation from A. Humboldt, whose notice he had already attracted, and to whom, in the form of letters, many of his afterwards published communications were made. Notwithstanding the direction given to his energies by his technical education and engagements, his natural bent soon showed itself, and we find him making observations on the meteorology

and the vegetation of the regions he visited. In regard to his contributions to science while in South America, Humboldt speaks of him as having enriched chemistry, meteorology, astronomy, and geography, with a number of precious works.

On his return to France, Boussingault was appointed Professor of Chemistry at Lyons, where he conducted an investigation on the composition of the atmosphere. He married the sister of a former fellow student at St. Étienne, M. Le Bel; and by his marriage became joint proprietor, with his brother-in-law, of the now famous estate of Bechelbronn, in Alsace, which besides a large farm included a mine of bitumen. M. Le Bel, besides being a chemical manufacturer, was also a very intelligent practical farmer, who was accustomed to use the balance for the weighing of manures, crops, and cattle. Here, then, was associated "practice with science," and it was under these favourable, not to say indispensable conditions, that the first laboratory on a farm was established, and the first agricultural experimental station was founded.

From this time forward, Boussingault generally spent about half the year in Paris, and the other half in Alsace. His first important contribution to agricultural chemistry was made in 1836, when he published a paper on the quantity of nitrogen contained in different foods, and on the equivalents of the foods, founded on the amount of nitrogen they contained, which he determined in a large series of such foods; and he compared the estimates so arrived at with the results of others founded on actual experience. Although his original conclusions have, probably, undergone some modification, the work itself marked a great advance on previously existing knowledge and modes of viewing the subject.

In 1837 Boussingault published papers on the amount of gluten in different kinds of wheat, on the influence which the clearing of forests exercises in diminishing the flow of rivers, and on the meteorological influences affecting the culture of the vine. In 1838 he published the results of an elaborate research on the principles underlying the value of a rotation of crops. He determined by analysis the composition, both organic and mineral, of the manures applied to the land, and of the crops harvested; and in his treatment he evinced a clear perception of the most important problems involved in such an inquiry, some of which, even with the united labours of himself and many other workers, have scarcely yet received an undisputed solution. Thus, in the same year he published the results of an investigation on the question whether plants assimilate the free nitrogen of the atmosphere; and although the analytical methods of the day were inadequate to the decisive settlement of the point, his conclusions were in the main those which much subsequent work of his own,

and much of others also, has served to confirm. As a further element in the question of the chemical statistics of a rotation of crops, Boussingault determined the amount and composition of the residues of crops. He also ascertained the amount of constituents consumed in the food of a cow and a horse, as against the amount yielded in the milk and excrements of the cow, and in the excrements of the horse. Here, again, the exigencies of the investigation he undertook were beyond the reach of the known methods of the time. Indeed, rude as the art of agriculture is generally considered to be, the scientific elucidation of its practice requires the most refined and varied methods of research, dealing as the subject does with the chemistry of the atmosphere, of meteoric and other waters, of the soil, of vegetation, and of animal life; and a characteristic of the work of Boussingault may be said to be that he has frequently had to devise methods suited to his purpose before he could grapple with the problems before him; and in this way he has made valuable contributions to analytical chemistry.

In 1839, chiefly in recognition of his important contributions to agricultural chemistry, Boussingault was elected a member of the Institute. Thus, already before 1840, the date of the first appearance of Liebig's memorable work, Boussingault had canvassed much of the ground, and there can be no doubt that many of the important facts established by his researches served as the basis for many of Liebig's brilliant generalisations. This led to the publication, in 1841, by Dumas and Boussingault jointly, of an essay, which was afterwards translated into English, and published in this country under the title of "The Chemical and Physiological Balance of Organic Nature." In 1843, Boussingault published a larger work, which embodied the results of many of his own previous original investigations. This also was translated and published in this country, under the title of "Rural Economy in its Relations with Chemistry, Physics, and Meteorology." A second edition of this book, *Économie Rurale*, appeared in France in 1857, but was not translated into English.

Although Boussingault's attention has been by no means limited to subjects bearing on agriculture, by far the greater number of his researches have had relation to the problems which it suggests. Thus the amount and condition of the combined nitrogen in the atmosphere, in the aqueous depositions from it in rivers and springs, and in the soil, have been investigated by him. The amounts of nitrogen, phosphoric acid, &c., in different manuring substances have been determined, and their comparative values estimated accordingly. The question of whether or not plants assimilate the free nitrogen of the air has again and again been taken up, the weight of the evidence

always serving to confirm the conclusion that they do not. In a letter to Dr. Gilbert, written in 1876, he says: "If there is one fact perfectly demonstrated in physiology, it is this of the non-assimilation of free nitrogen by plants; and I may add, by plants of an inferior order, such as mycoderms and mushrooms." And in conversation with Dr. Gilbert, at Liebfrauenberg, in 1883, he still emphatically maintained the same view. Recently he made experiments in regard to some functions of the leaves of plants. Lastly, in the sphere of animal chemistry, he from time to time devoted himself to the elucidation of important points, such as the sources in the food of the fat of the fattening animal, the assimilation of mineral constituents, the question whether any of the nitrogen of the food of the animal is exhaled, and so on.

In 1844 Boussingault was elected a member of the Conseil d'Hygiène Publique, and in this capacity carried out numerous investigations on questions both of general hygiene and of the special hygiene of various chemical industries.

In 1848 Boussingault, who was in politics a moderate Republican, was elected a member of the Assemblée Nationale, and he was for a short time member of the Conseil d'État. In 1851, however, he was on account of his political opinions, dismissed by the Government from his position of Professor at the Conservatoire des Arts et Métiers; but on the representation of scientific friends of eminence and authority, and the threat of his colleagues to resign in a body, he was reinstated.

When, in the commencement of the Franco-German War, the Crown Prince of Prussia had crossed the Rhine into Alsace, some of the soldiers bivouacked in the woods of Bechelbronn, and some of the officers were quartered in Boussingault's house, the old convent of Liebfrauenberg. Some time afterwards Boussingault received a letter from one of those officers, saying that, finding in whose house they were, and having the highest respect for its scientific owner, he had done his best, he hoped successfully, to prevent any injury from being done, especially to the laboratory. He further expressed a hope that Boussingault would find nothing missing, except a thermometer, which he had himself presumed to take as a memorial.

Boussingault's first scientific contribution appeared in 1821, and in the "Royal Society Catalogue of Scientific Papers" there is given a list of 150 papers published by him from that date to 1873 inclusive. Almost the whole, if not the whole, of Boussingault's investigations relating to agricultural chemistry will be found recorded in his work, entitled *Agronomie, Chimie Agricole et Physiologie*, published in seven volumes, the first of which appeared in 1860.

Boussingault was elected a Foreign Member of the Chemical

Society in 1849, and received the Copley Medal of the Royal Society in 1878.

He died at Paris on May 11th, 1887, in his eighty-sixth year.

Mr. Patrick Duffy, F.L.S., F.C.S., was born in 1829, and educated at the High School, Monaghan. In 1848 he obtained an appointment in the Inland Revenue Department, and two years later attended University College, London, for a course of instruction in chemistry, with the view of detecting adulterations in articles subject to the duties of Customs and Excise. Under Professors Graham and Williamson he diligently and most successfully pursued his studies, and in 1851 obtained the Gold Medal for Chemistry. He also made great advancement in other subjects, particularly in the German language and literature. On leaving University College, his official duties occupied a considerable portion of his time, but he continued to devote himself to the study of chemistry and botany.

Amongst his contributions to science was a paper on the transformation, &c., of fats, which is of considerable importance, and was published in the Quarterly Journal of the Société Chimique de Paris. He received great praise from scientific men for the industry and patience shown in the preparation of this work, particularly from the late Professor A. Wurtz, of Paris.

In 1856, he was again in London, and in that year obtained the University College Senior Gold Medal for Botany. About this time he distinguished himself by the detection of adulterations in taxed commodities.

He was afterwards stationed at Kilkenny for some years as Supervisor of Inland Revenue, and, in spite of his multifarious duties, contributed many interesting meteorological notices to the *Kilkenny Moderator*, and did work in connection with the Irish Historical and Archæological Society, of which he was a member for many years.

Although a man of considerable scientific attainments, and a good linguist, few of his papers have appeared in print. He was constantly at work on some subject, and availed himself of every available opportunity to obtain information in connection with scientific and social matters. During his visits to the Continent, he collected valuable particulars respecting the cultivation of hops, &c., the manufacture of beer and other alcoholic liquors, and articles on which duties were levied. In his travels he obtained numerous botanical specimens, of which he had a considerable collection.

He died very suddenly on the 27th May, 1887.

Thomas Samuel Humpidge was born at Gloucester on July 23rd, 1853, and received his early training at the Crypt Grammar School in that town. Whilst at school he won a number of prizes, and

already showed a strong inclination towards those sciences, the study and furtherance of which later on formed the great aim of his life. Unfortunately the necessity of earning a livelihood compelled him to leave school at the age of fourteen, when he entered the employment of a Gloucester corn merchant, with whom he remained for seven years. While thus engaged, he had little spare time, and, consequently, did not make such rapid progress in his scientific studies as he would have done under more favourable circumstances; the time he could get to himself, however, he devoted to science, attending many of the classes at the Science and Art Schools. Mr. Walter Jeffery, then at the head of the science department of these schools, recognised the ability of his young student, and did all he could to foster it. At this time, young Humpidge obtained permission to appropriate a loft in his father's house, and this he gradually converted into a rough laboratory in which to supplement his work at the Science Schools. In after life he looked back with pleasure to his connection with these Schools, and always retained a loving and grateful remembrance of his first science teacher and friend, whilst on the other hand Mr. Jeffery (who survives his former pupil) followed the latter's career with the warmest interest. To show what good use he made of his spare time, it may be mentioned that in one year he sat for examination in seventeen branches of science at the May examinations, passing successfully in thirteen or fourteen thereof.

In 1873 he obtained from the Science and Art Department the silver medal for geology, receiving at the same time the offer of free lectures and laboratory work at the Royal School of Mines, and £50 a year for two years. Though unable to avail himself of this offer at the time, he accepted it when renewed in the following year.

His strictly scientific training may thus be said to have begun in the autumn of 1874, when he entered at the Royal School of Mines, making chemistry his chief subject. Here he obtained a bronze medal, and in 1875 was nominated to one of the three Jodrell travelling scholarships founded at that time. Whilst studying here under Professor Frankland, he carried out a valuable research on "The Coal-gas of the Metropolis," the results of which were published in this Journal. In the same year, he passed the Intermediate B.Sc. at London, gaining the second place in the first class in Honours and an exhibition of £40 a year for two years.

In 1876, Humpidge went to Heidelberg, where for two years he studied under Bunsen, and became an ardent and enthusiastic disciple of that great chemist. During this time he devoted his energies to the investigation of the rare earths, and in 1879, in conjunction with his friend and fellow student Mr. W. Burney, communicated the results obtained to this Society.

At Heidelberg he took the degree of Ph.D. (*summâ cum laude*), and about the same time passed his final B.Sc. examination.

In the spring of 1878, he removed to the Fellenberg Institute, Hefwyl, near Berne, where he had been appointed Science Master; here he was very successful in his teaching, and soon won the love and esteem of both pupils and colleagues. In September, 1879, he was elected to the Chair of Natural Science in the University College of Wales, Aberystwyth, which post he retained till his death.

At the time of his appointment, the resources of the Science Department of the college were very limited, and for the first five terms of his tenancy of the chair he was single-handed, being responsible for the whole of the science teaching of the college, and having but poor laboratory accommodation and a scanty supply of apparatus. Notwithstanding, he threw his whole heart into the work, and the present successful position of the Science Department there is undoubtedly due in large measure to Professor Humpidge's enthusiasm and devotion, and its gradual growth and development was a constant source of the keenest enjoyment to him. A lecturer in Biology, and subsequently one in Physics were added to the college staff, and Dr. Humpidge was thus enabled to devote his whole energies to the teaching of chemistry.

Naturally, under these circumstances, his powers were severely taxed by the duties of the chair, but he still managed to work in his favourite fields of chemical research, though, it is to be feared, at considerable sacrifice of health. Whilst at Aberystwyth, he devoted himself to the determination of the atomic weight, and the position in the atomic system of the rare element—beryllium. This problem he attacked from two points of view, namely, by the determination of the specific heat of the element and by the determination of the vapour-densities of its compounds. It is not necessary to dilate here on the difficulties of such work which are sufficiently well known to Fellows of this Society. His first specific heat determinations led him to adopt the atomic weight 13·6, and his early attempts to determine the vapour-densites of the haloïd salts proved abortive owing to the high temperature at which they are volatile, their easy decomposition, and their corrosive action on glass. When, after long, laborious, and careful work he was ready in the spring of 1884 to renew his experiments in platinum vessels, and under more favourable conditions, he heard that the two well-known Swedish chemists—Nilson and Pettersson—were at work on the same subject, and about to publish their results. Great as was the temptation to hurry on his work, he would not permit his private research to interfere in the least with the duties of his chair, and so quietly allowed his experiments to lie in abeyance till the long vacation, though he well knew that this

would entail loss of priority of publication. But love of the truth was his great aim and incentive, and he was content to finish and publish his experiments as independent confirmation of his friendly rivals' results. Not by any means the least pleasing feature of this incident was the friendly spirit existing between Dr Humpidge and the two Sedwish chemists, and the letters which passed between them and the references to one another in their respective papers are very pleasant reading and in very welcome contrast to the bitter rancour but too often found between rival investigators. The results of his determinations of the vapour-densities of beryllium chloride, and his new determinations of the specific heat of the metal, were communicated from time to time by Dr. Humpidge to the Royal Society in four papers, of which one was published in the *Philosophical Transactions* and three in the *Proceedings;* the results obtained fully confirmed and established the atomic weight of beryllium as 9·1.

Towards the expense of his work on beryllium, the Royal Society made, from the Research Fund, two grants of £50 each and one of £20, and with the elaborate and accurate calorimeter which he had thus been enabled to construct for his specific heat determinations of beryllium, Dr. Humpidge intended to make a series of redeterminations of this important physical factor with other elements. With this object, he had prepared very pure specimens of copper, magnesium, and tin, and was preparing others when the sad fire of July, 1885, occurred by which the college was almost wholly destroyed, and in which Dr. Humpidge not only lost his apparatus and materials but also valuable notes of much work already completed.

The terrible night of the fire, in which Humpidge but narrowly escaped death, undoubtedly greatly injured his health; but with his usual ardour he at once decided to forego his much-needed vacation, devoting it to the arrangement of temporary science premises. He continued the duties of his chair during the following session and also reconstructed his calorimeter, &c., but towards the end of the session his health began to give way and the long vacation did not bring the hoped-for improvement, so that in September, 1886, he had to obtain leave of absence from his Professorial duties. He spent the winter in Nice and San Remo, and the spring seemed to bring renewed vigour. So much was this the case, that Professor Humpidge returned to Aberystwyth in August, 1887, with the full intention of resuming work at the commencement of the autumn session. A relapse, however, again occurred, and after a painful illness he died of cerebral deterioration on November 30th.

His friends did not wish an ostentatious funeral, but the unanimous desire of colleagues and students to pay a last tribute of esteem to a valued and loved friend and teacher was not denied. The burial

therefore took place with academic honours, representatives of the staff having the mournful pleasure of acting as pall-bearers at the house, whilst students had the privilege of performing the same duties in the pretty churchyard of Llangoewen (about two miles from Aberystwyth) where his body was laid in the grave. The funeral cortege as it wound slowly over the hills, preceded by the whole of the college staff of students in their sombre academic garb, formed a touching and picturesque though mournful scene which will long remain in the memory of those who took part in or witnessed it. The ceremony at the grave was simple and touching, and when, as the coffin was lowered into the grave, the whole of those present sang reverently the quaint but solemn Welsh Resurrection hymn, "Bydd myedd o ryfeddodan," many an eye was moist.

During the last year of his work at the college, Dr. Humpidge gave great care and thought to the elaboration of the plans for the new laboratories, and this, resumed as soon as his strength began to return on the sunny shores of the Mediterranean, was continued to the last. After his return to Aberystwyth (when the work of rebuilding had already begun), it was Professor Humpidge's greatest pleasure to lie at his study window and watch the steady progress of the buildings of which to the end he fondly spoke as "my laboratory."

As a teacher he very soon won the regard of his students at Aberystwyth, and there are not a few of them who are now making their way in the scientific world, who would freely admit the enthusiasm and ardour of their old teacher to have given them their first stimulus to a scientific career. By his colleagues, he was equally esteemed as a friend, as a teacher, and as a fellow councillor in the deliberations of the Senate.

But his influence on the scholastic world was not confined to Aberystwyth. His translation of Kolbe's *Inorganic Chemistry* rapidly won favour as a text-book, and a new edition had been called for, and almost perfected, at the time of Professor Humpidge's death.

Shortly after he went to Aberystwyth, Dr. Humpidge married Fräulein Johanna Ruder of Oldenburg, whose acquaintance he had made whilst at Hefwyl. He leaves two boys of the tender ages of five and three respectively.

Owing to the heaviness of his college duties and to the difficulty of access of Aberystwyth, his face was seen at the Society's meetings with much less frequency than he or his friends could have wished. But there are still many among us who will feel they have lost in him a valued and true friend and fellow worker, and many more to whom, though personally unknown, his work has made him no stranger.

Amongst the obituary notices of deceased Fellows issued in 1886, the name of Mr. W. Sykes Ward occurred. As no further information was supplied to the Society at that time, no biographical notice could be given. But the exceptional circumstances of Mr. Ward's early association with the Chemical Society, and the retention of that connection for about 38 years, make it desirable briefly to supply the omission.

Mr. W. Sykes Ward, of Leeds, was a solicitor whose tastes always inclined him in the direction of physical science, and he was able to devote both leisure and means towards such pursuits.

In Vol. I of the *Quarterly Journal of the Chemical Society*, a paper by Mr. Ward, "On a Balance Galvanometer," is mentioned as the fourth in order read before the Chemical Society (on December 4, 1848), which, at that period, only published "at irregular intervals" communications made to it. In Vol. II (1850) this paper is printed, and the presentation of the galvanometer to the Society is acknowledged. The suggested method for the measurement of an electrical current was ingenious, and differed from that put forward by Becquerel in 1837, which probably was unknown to Mr. Ward.

Mr. Ward was an early explorer in such fields as telegraphy, atmospheric railways, photography, &c., and his inventions were the subject of several patents. He was an enthusiastic student of music in its higher aspects.

For about 30 years Mr. Ward was one of the Honorary Secretaries of the Leeds Philosophical and Literary Society, whose operations were most congenial to the great versatility of his tastes for science. Owing to failing health, Mr. Ward spent the last few years of his life in retirement, continuing, however, his scientific pursuits. The larger part of his considerable collection of scientific apparatus has been transferred by his family to the Physics Department of the Yorkshire College at Leeds.

XXXIX.—*The Constitution of certain so-called "Mixed Azo-compounds."*

By Francis R. Japp, LL.D., F.R.S., and Felix Klingemann, Ph.D.

Part I. Introductory and Theoretical.

Between three and four years ago, Dr. Ludwig Landsberg mentioned to one of us that he had obtained by the action of sodium methoxide and methyl iodide on benzene-azo-acetone* a colourless, feebly basic compound, melting at 64°, which he had not further examined. Dr. Landsberg stated that he did not intend to continue the investigation of this compound, and very kindly allowed us to take up the subject.

Analysis showed us that, as was to be expected, the compound had been formed from benzene-azo-acetone by the substitution of a methyl-group for hydrogen. Adopting the usually accepted formula for benzene-azo-acetone,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}N{:}N{\cdot}C_6H_5,$$

the most probable supposition was that the methyl had displaced a hydrogen-atom of the methylene-group—a view which we put forward in a preliminary note on the subject (*Ber.*, **20**, 3398). By the action of acetic anhydride on benzene-azo-acetone, we also prepared an acetyl-derivative, to which we assigned (*loc. cit.*) an analogous constitution. We shall show in the present communication, that the above formula for benzene-azo-acetone does not correctly express its constitution, and that the formulæ which we ascribed to the two derivatives just mentioned must be correspondingly modified.

As the yield of the methyl-derivative obtained by Dr. Landberg's reaction was very small,† we endeavoured to prepare the compound by splitting off carbon dioxide from benzene-azo-methacetoacetic acid, a method which would at the same time prove its constitution. We had hoped to obtain ethylic benzene-azo-methacetoacetate by the action of diazobenzene chloride on ethylic sodio-methacetoacetate, following the analogy of the reaction described by V. Meyer (*Ber.*, **10**, 2075) for the preparation of ethylic benzene-azo-acetoacetate from ethylic acetoacetate and diazo-salts; but we found that the benzene-azo-group could only be introduced into the molecule of ethylic

* Benzene-azo-acetone, first described by v. Richter and Münzer (*Ber.*, **17**, 1928), was discovered independently by Dr. Landsberg in the Chemical Laboratory of the Normal School of Science about the time referred to; but the investigation was abandoned after the publication of v. Richter and Münzer's memoir.

† A relatively advantageous method of carrying out the reaction is described later on.

methacetoacetate with simultaneous elimination of the acetyl-group: thus—

$$CH_3\cdot CO\cdot CNa(CH_3)\cdot COOC_2H_5 + C_6H_5\cdot N_2Cl + H_2O = C_{11}H_{14}N_2O_2 + C_2H_4O_2 + NaCl.$$

To the "ester" thus formed we at first assigned the formula—

$$CH_3\cdot \underset{\displaystyle N:N\cdot C_6H_5}{\overset{\displaystyle |}{C}}H\cdot COOC_2H_5$$

(*Ber.*, **20**, 2942), regarding it as the ethyl salt of *benzene-α-azopropionic acid*—the first representative of a new class of benzene-azo-fatty acids. The acid, $C_9H_{10}N_2O_2$, was obtained by hydrolysis; and we also prepared a number of homologous "esters" and acids, under the impression that we were dealing with a new class of compounds.

The supposed benzene-azo-propionic acid, $C_9H_{10}N_2O_2$, yielded, by treatment with sodium amalgam, *benzene-hydrazopropionic acid*,

$$CH_3\cdot \underset{\displaystyle NH\cdot NHC_6H_5}{\overset{\displaystyle |}{C}}H\cdot COOH$$

which proved to be identical with E. Fischer and Jourdan's "phenylhydrazinepropionic acid" (*Ber.*, **16**, 2244), a fact which, however, escaped our notice at the time of our first publications on the subject (*Ber.*, **20**, 2943 and 3284). Fischer and Jourdan obtained their acid by reduction of phenylhydrazonepyruvic acid,*

$$CH_3\cdot \underset{\displaystyle \ddot{N}\cdot NHC_6H_5}{\overset{\displaystyle ||}{C}}\cdot COOH$$

On comparing our "benzene-azo-propionic acid" with phenylhydrazonepyruvic acid, we found that these two acids were also identical. It was, therefore, necessary to ascertain whether the acid had the constitution of a hydrazone, as assumed by Fischer and Jourdan, and indicated by its formation from phenylhydrazine and pyruvic acid; or that of an azo-compound, as we had all along supposed. The fact that in the reaction discovered by us, the diazo-salt expels simultaneously sodium and acetyl from the molecule of ethylic sodio-methacetoacetate might, it appeared to us, be interpreted in favour of the hydrazone formula, since in this process the bivalent group, $CH_3\cdot \underset{\displaystyle \ddot{}}{C}\cdot COOC_2H_5$, would be formed; on the other hand, the possibility of regenerating the acid by the action of an ammoniacal solution of a cupric salt on benzene-hydrazopropionic acid as observed

* In the nomenclature of compounds formed by the action of phenylhydrazine on carbonyl-compounds we have followed the recently published suggestion of Emil Fischer (*Ber.*, **21**, 984).

by Fischer and Jourdan, indicated rather the constitution of an azo-compound. The problem, we pointed out, was of the same order as that involved in distinguishing between an isonitroso- and a nitroso-compound (*Ber.*, **20**, 3285).

Of course the question also arose, as to whether benzene-azo-acetone itself was an azo-compound or a hydrazone; and it appeared likely that in the case of this compound a study of the alkyl-derivatives obtainable by Landsberg's reaction might furnish a ready solution of the problem. If benzene-azo-acetone was an azo-compound, the alkyl-derivative would have the formula—

$$CH_3{\cdot}CO{\cdot}CHR'{\cdot}N{:}N{\cdot}C_6H_5;$$

whereas, if it was a hydrazone (derived from pyruvic aldehyde), the alkyl would more probably attach itself to nitrogen: thus—

$$CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N{<}\begin{matrix}C_6H_5\\R'\end{matrix}.$$

By the action of nascent hydrogen, an alkyl-derivative of the first formula ought to yield aniline; one of the second formula, an alkyl-aniline. In either case, the other half of the molecule would probably yield acetone.

The method of attacking the problem was therefore analogous to that employed by Victor Meyer and Ceresole in ascertaining the constitution of the isonitroso-compounds (*Ber.*, **15**, 3071).

We preferred, however, to introduce, instead of a alkyl-group, the group $\cdot CH_2{\cdot}COOH$, into the molecule of benzene-azo-acetone. The resulting compound would thus yield on reduction, instead of a mixture of two bases, a base and an acid, in this way greatly facilitating the separation of the products; whilst, in order to ascertain the constitution of the compound, it was only necessary to distinguish between aniline, on the one hand, and anilidoacetic acid on the other, instead of between aniline and an alkyl-aniline.

Benzene-azo-acetone was accordingly heated with sodium ethoxide and ethylic chloracetate in alcoholic solution. The resulting "ester" was converted into the acid, which proved to have the expected formula, $C_{11}H_{12}N_2O_3$. On reduction, this acid yielded anilidoacetic acid, but no aniline. It has therefore the formula—

$$CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N{<}\begin{matrix}C_6H_5\\CH_2{\cdot}COOH\end{matrix};$$

and "benzene-azo-acetone" is not an azo-compound at all, but a hydrazone of the formula—

$$CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}NHC_6H_5,$$

—an "aldehydrazone" of pyruvic aldehyde, as distinguished from the "ketohydrazone"* derivable from the same compound.

This view was confirmed by the fact that "benzene-azo-acetone" yielded with phenylhydrazine a compound—

$$\begin{matrix} CH_3\cdot C\!:\!N\cdot NHC_6H_5 \\ CH\!:\!N\cdot NHC_6H_5, \end{matrix}$$

identical with the osazone† of pyruvic aldehyde (methylglyoxal) prepared by v. Pechmann.

It appears, therefore, that when diazo-salts act on ethylic acetoacetate and its analogues, or on their mono-alkylated derivatives, hydrazones are formed. R. Meyer (*Chem.-Zeit.*, 1887, 836) has shown that the compound obtained from ethylic malonate and diazobenzene chloride is identical with the phenylhydrazone of ethylic mesoxalate, but draws the opposite conclusion to that arrived at by us, believing that the hydrazone undergoes transformation into an azo-compound.‡

* These names are formed on the analogy of "aldoxime" and "ketoxime." "Aldehydrazone" is a contraction for "aldehydehydrazone."

† "Osazone" is the term introduced by Fischer to denote the dihydrazone of an α-dicarbonyl-compound.

‡ This preliminary communication in the *Chemiker-Zeitung* had unfortunately escaped our notice at the time we published our first note on the identity of our "benzene-azo-propionic acid" with Fischer and Jourdan's phenylhydrazonepyruvic acid.

Our views on the constitution of the above "mixed azo-compounds," were first published, together with a brief account of the experimental proofs, in the Proceedings of December 15, 1887, and somewhat later in the *Berichte* (**20**, 3284 and 3398). Professor Victor Meyer, who arrived independently at the same conclusions, published a paper later still in the *Berichte* (**21**, 11), in which he discusses the theoretical question very fully, but does not contribute any fresh experimental material, although he suggests various experiments, some of which we had already described in our paper. After his paper had been sent to the *Berichte* (date of reception, 30th December, 1887), Professor Victor Meyer received the number of the Proceedings containing the account of our work, and despatched to the *Berichte* an addendum (4th January, 1888) in which he says: "Ich gestatte mir, darauf hinzuweisen, dass ich über das Thema am 13. December in der Göttinger chemischen Gesellschaft vorgetragen habe."

We believe that, in the above sentence, Professor Victor Meyer has unintentionally conveyed the impression that he *read a paper* before the Göttingen Chemical Society on December 13. We understood the words in this sense, and therefore turned to the account of the meeting in question, given in the *Chemiker-Zeitung* (1887, **11**, 1584), but found no mention of any such paper. Later, however, on January 8, in the number of the *Chemiker-Zeitung* following that in which an account of our work had been published, there appeared a *second* and "supplementary" notice of the above meeting of the Göttingen Chemical Society, in which it was stated that, in a discussion which followed on the reading of a paper by P. Jacobsen, Professor Victor Meyer had made certain remarks on the constitution of mixed azo-

The bivalent hydrazone-group, $:N\cdot NHC_6H_5$, thus corresponds with the bivalent isonitroso-group, $:N\cdot OH$. The isonitroso-compounds, as Victor Meyer has shown, are formed either by the action of hydroxylamine on a carbonyl-compound, or by the action of nitrous acid on a compound containing the group CH_2 or CHR' attached to two electronegative radicles, R' being a readily displaceable radicle (acetyl or carboxyl). Substituting, in the foregoing statement, "phenylhydrazine" for "hydroxylamine," and "diazo-compound" for "nitrous acid," it describes the modes of formation of the hydrazones.

The analogy between the action of hydroxylamine and phenylhydrazine on carbonyl-compounds needs no illustration. The analogy between the action of nitrous acid and diazobenzene-compounds on ethylic acetoacetate, acetoacetic acid and their monalkyl-derivatives, is exemplified in the following equations, in which, for the sake of simplicity, free diazobenzene is employed, instead of its salts:—

1. With ethylic acetoacetate the reactions may be expressed as follows:—

$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + HNO_2 = CH_3\cdot CO\cdot \underset{\ddot{N}\cdot OH}{C}\cdot COOC_2H_5 + H_2O,$$

$$\text{and } CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + C_6H_5\cdot N_2HO = CH_3\cdot CO\cdot \underset{\ddot{N}\cdot NHC_6H_5}{C}\cdot COOC_2H_5 + H_2O.$$

2. In the case of monalkyl-derivatives of ethylic acetoacetate, the acetyl-group is expelled:—

$$\begin{matrix} CH_3\cdot CO \\ CH_3 \end{matrix}\!\!>\!CH\cdot COOC_2H_5 + HNO_2 = CH_3\cdot \underset{\ddot{N}\cdot OH}{C}\cdot COOC_2H_5 + C_2H_4O_2,$$

$$\text{and } \begin{matrix} CH_3\cdot CO \\ CH_3 \end{matrix}\!\!>\!CH\cdot COOC_2H_5 + C_6H_5\cdot N_2HO = CH_3\cdot \underset{\ddot{N}\cdot NHC_6H_5}{C}\cdot COOC_2H_5 + C_2H_4O_2.$$

compounds. The views embodied in these remarks were, we may say, identical with those put forward by us, and to this extent we were forestalled by Professor Victor Meyer.

Two criticisms suggest themselves on the foregoing.

In the first place, as regards the general question, although a discussion made before a learned Society may embody valuable remarks, yet if this discussion is not reported in the ordinary course along with the other work of the Society, it would be hardly fair to outsiders to regard such remarks as equivalent to publication.

Secondly, on the present and personal matter, if we had chosen to take the same course as Professor Victor Meyer, and publish our theoretical views first, leaving the experimental confirmation for later, we might have considerably anticipated the date of December 13, on which he lays so much stress.

3. When nitrous acid acts on free acetoacetic acid, or its monalkyl-derivatives, instead of on their ethyl salts, the carboxyl-group is eliminated, and isonitroso-ketones are formed. We find that in this case also diazobenzene behaves in an analogous manner. Thus, with acetoacetic acid, we have—

$$CH_3\cdot CO\cdot CH_2\cdot COOH + HNO_2 = CH_3\cdot CO\cdot CH{:}N\cdot OH + CO_2 + H_2O,$$

and

$$CH_3\cdot CO\cdot CH_2\cdot COOH + C_6H_5\cdot N_2HO = CH_3\cdot CO\cdot CH{:}N\cdot NHC_6H_5 + CO_2 + H_2O;$$

whilst methacetoacetic acid yields with diazobenzene the compound $CH_3\cdot CO\cdot C(CH_3){:}N\cdot NHC_6H_5$ (the monohydrazone of diacetyl, already prepared by v. Pechmann from diacetyl and phenylhydrazine); and ethacetoacetic acid yields the corresponding compound of the formula $CH_3\cdot CO\cdot C(C_2H_5){:}N\cdot NHC_6H_5$.

The so-called azo-ketones are thus monohydrazones of α-dicarbonyl-compounds. We also discovered, in the course of the present investigation, the following curious mode of formation of osazones (dihydrazones of α-dicarbonyl-compounds).

In heating phenylhydrazonepyruvic acid at 180—190°, until it had ceased to evolve gas, we obtained, along with oily matters, a crystalline substance of the formula $C_{16}H_{18}N_4$ (*Ber.*, **20**, 2943). We afterwards found that this compound was identical with the osazone of diacetyl, since prepared by v. Pechmann. Its formation from phenylhydrazonepyruvic acid may be expressed by the equation—

$$2C_9H_{10}N_2O_2 = C_{16}H_{18}N_4 + 2CO_2 + H_2;$$

but we believe that it is in reality formed in a secondary reaction. E. Fischer and Jourdan have shown (*Ber.*, **16**, 2242) that phenylhydrazonepyruvic acid breaks up on heating, with evolution of carbon dioxide and formation of aldehydrazone (ethylidenephenylhydrazine)—

$$C_9H_{10}N_2O_2 = C_8H_{10}N_2 + CO_2.$$

In fact, this is the chief reaction, the oily substance which we obtained consisting mainly of aldehydrazone, whilst the osazone is formed only in small quantity.

We, therefore, heated aldehydrazone at 180—190°, and found that the osazone of diacetyl was formed. The following equation shows the reaction:—

$$\begin{matrix} CH_3\cdot C\boxed{H}{:}N\cdot NHC_6H_5 \\ CH_3\cdot C\boxed{H}{:}N\cdot NHC_6H_5 \end{matrix} = \begin{matrix} CH_3\cdot C{:}N\cdot NHC_6H_5 \\ CH_3\cdot C{:}N\cdot NHC_6H_5 \end{matrix} + H_2.$$

Part II. Experimental.

1. *Introduction of Monad Radicles into the Molecule of Pyruvaldehydrazone* ("*Benzene-azo-acetone*").

The pyruvaldehydrazone (to give the compound the name denoting the constitution to which the following experiments point) was prepared by a modification of v. Richter and Münzer's method (*Ber.*, **17**, 1928). The crude product of the action of diazobenzene chloride on ethylic sodacetoacetate was first hydrolysed by warming for a few minutes with alcoholic caustic soda. Instead, however, of continuing the heating until the sodium salt thus formed was converted by the action of the caustic alkali into pyruvaldehydrazone and sodium carbonate, we added water, acidified with hydrochloric acid so as partially to precipitate the organic acid, added sodium carbonate so as to redissolve the precipitate, and then heated the liquid on a water-bath for several hours. In this way, the pyruvaldehydrazone was not exposed to the decomposing action of the caustic alkali, and was obtained in a purer condition. It separated from the hot liquid in large plates, which were filtered off, and the liquid was heated afresh until no further separation occurred. The latter portions were less pure. The compound is most conveniently purified by recrystallisation from hot benzene or methyl alcohol. As regards its physical properties, we have nothing to add to v. Richter and Münzer's description.

We have described the foregoing method because it was that by which the material employed in this investigation was obtained, but later on we give a method by which the compound can be much more readily prepared, namely, by the action of diazobenzene chloride on acetoacetic acid.

Action of Acetic Anhydride.—Pyruvaldehydrazone was boiled with excess of acetic anhydride for several hours, after which the solution was poured into water. An oil separated, which speedily became crystalline. By recrystallisation from boiling light petroleum, the compound was obtained in colourless needles melting at 93°. From a benzene solution, it is deposited in thick well-formed crystals, apparently quadratic. Analysis agreed with the formula $C_{11}H_{12}N_2O_3$.

	Substance.	CO_2.	H_2O.
I.....	0·2150	0·5105	0·1151
II.....	0·2265	0·5375	0·1202

III. 0·1110 gram, burnt with oxide of copper in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 19·5° and under 459 mm. pressure. After absorption of the nitric oxide there remained 22·63 c.c. of dry nitrogen at 19·5° and under 434 mm. pressure.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found. I.	II.	III.
C	64·70	64·75	64·72	—
H	5·88	5·94	5·89	—
N	13·73	—	—	14·05
O	15·69	—	—	—
	100·00			

The compound is therefore *acetylpyruvaldehydrazone*,

$$CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N(C_2H_3O)C_6H_5.$$

At the time when we first prepared this compound, we were under the impression that the acetyl-group had displaced hydrogen in the "methylene-group of benzene-azo-acetone" and that the compound was therefore a diketone. We consequently heated it with an excess of phenylhydrazine in alcoholic solution, but even at 200° only one oxygen-atom was displaced by the phenylhydrazone-group. The phenylhydrazone, which in reality has the formula

$$\begin{matrix} CH{:}N{\cdot}N(C_2H_3O)C_6H_5 \\ CH_3{\cdot}C{:}N{\cdot}NHC_6H_5 \end{matrix},$$

crystallises in pale-yellow needles, melting at 229°, readily soluble in hot, sparingly soluble in cold alcohol.

0·1013 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15·5° and under a pressure of 548 mm. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 15·5° and under 543 mm. pressure.

	Calculated for $C_{17}H_{16}N_4O$.	Found.
N in 100 parts	19·04	19·06

Action of Methyl Iodide.—By heating together, in methyl alcoholic solution, equimolecular proportions of pyruvaldehydrazone, sodium methoxide, and methyl iodide, only a very small proportion of the pyruvaldehydrazone was converted into the methyl-derivative. This is due to the fact that the sodium methoxide and methyl iodide interact in great part by themselves, as if no pyruvaldehydrazone were present. We then tried whether an increase in the proportion of sodium methoxide and methyl iodide would render the conversion more complete; but the result was still unsatisfactory. The following slight modification of the process, however, by which the presence of any but a very small proportion of sodium methoxide during the progress of the reaction is avoided, gave an excellent yield.

A solution of 1 mol. proportion of pyruvaldehydrazone with 4 mol.

proportions of methyl iodide in methyl alcohol was boiled with a reflux condenser; a solution of 4 atomic proportions of sodium in methyl alcohol was allowed to drop gradually into the boiling liquid, so that the process extended over several hours; and the boiling was continued for a short time after the whole of the methoxide had been added. On pouring the contents of the flask into excess of water, an oil separated which speedily solidified; this substance was purified by recrystallisation from boiling light petroleum. It forms colourless, flat needles, melting at 64°, very soluble in alcohol, ether, and benzene, somewhat less soluble in light petroleum. It is a weak base, dissolving in concentrated hydrochloric acid, but is reprecipitated by water.

Analysis showed that it had the formula $C_{10}H_{12}N_2O$:—

	Substance.	CO_2.	H_2O.
I.....	0·2180	0·5450	0·1344
II.....	0·2039	0·5098	0·1260

III. 0·1088 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of nitrogen, measured dry at 18·2° and under 500 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{10}H_{12}N_2O$.	Found.		
		I.	II.	III.
C	68·18	68·18	68·18	—
H	6·82	6·85	6·86	—
N	15·91	—	—	16·12
O	9·09	—	—	—
	100·00			

The compound has the constitution $CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N{<}^{C_6H_5}_{CH_3}$.

That the methyl-group has not displaced hydrogen attached to carbon is shown by the fact that the compound is distinct from the hydrazone of diacetyl (*vide infra*).

When heated with phenylhydrazine in alcoholic solution, it yields a compound,

$$\begin{matrix} CH{:}N{\cdot}N(CH_3)C_6H_5 \\ CH_3{\cdot}C{:}N{\cdot}NHC_6H_5 \end{matrix},$$

which crystallises in faint-yellow needles, melting at 151—152°, sparingly soluble in alcohol, readily soluble in ether.

0·0770 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15·4° and under a pressure of 471 mm. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 15·6° and under 460 mm. pressure.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N in 100 parts	21·05	21·4

Action of Ethyl Iodide.—Pyruvaldehydrazone reacted in an analogous manner with sodium ethoxide and ethyl iodide, yielding the compound $CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N(C_2H_5)C_6H_5$, which crystallised from light petroleum in thin prisms, melting at 55°. The substance had a faint reddish tinge, doubtless due to impurity.

0·1942 gram gave 0·4923 gram CO_2 and 0·1277 gram H_2O.

	Calculated for $C_{11}H_{14}N_2O$.	Found.
C	69·47	69·13
H	7·37	7·30
N.	14·74	—
O.....	8·42	—
	100·00	

Action of Ethylic Chloracetate.—The pyruvaldehydrazone, together with four times its molecular porportion of ethylic chloracetate, was dissolved in alcohol, and a solution of 4 atoms of sodium in alcohol was gradually added to the boiling liquid, conducting the operation as in the preparation of the methyl-derivative. Caustic soda was then added, and the solution was boiled so as to hydrolyse the "ester" which had been formed in the reaction. After expelling part of the alcohol by heating, water was added, the liquid was filtered, and the new acid was precipitated with hydrochloric acid. In order to purify the substance, it was dissolved in a cold solution of sodium carbonate, reprecipitated with hydrochloric acid and repeatedly recrystallised from boiling water. It formed yellow needles which melted with decomposition about 161—162°. Analysis agreed with the formula $CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}N(C_6H_5)CH_2{\cdot}COOH$.

I. 0·2128 gram gave 0·4671 gram CO_2 and 0·1070 gram H_2O.

II. 0·1067 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16° and under 405 mm. pressure. After absorption of the nitric oxide there remained 22·63 c.c. of dry nitrogen at 16° and under 395 mm. pressure.

	Calculated for $C_{11}H_{12}N_2O_3$.	Found.	
		I.	II.
C	60·00	59·86	—
H	5·45	5·58	—
N	12·73	—	13·25
O	21·82	—	—
	100·00		

Action of Nascent Hydrogen on the Acid $C_{11}H_{12}N_2O_3$.—The acid was dissolved in alcohol and treated with excess of tin and hydrochloric acid. The tin was then precipitated with sulphuretted hydrogen, the solution evaporated to dryness, the residue extracted with ether,* and the substance remaining on evaporation of the ether recrystallised from hot water. The aqueous solution on cooling deposited small crystals, with a slight brownish tinge, melting at 126—127°. (M. p. of anilidoacetic acid 126—127°; P. Meyer). In all its properties, excepting the slight brown colour, it was indistinguishable from a specimen of anilidoacetic acid prepared from bromacetic acid and aniline. As the quantity was too small for further purification we analysed it direct.

0·0926 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15° and under 253 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 15° and under 246 mm. pressure.

	Calculated for $NH(C_6H_5)\cdot CH_2\cdot COOH$.	Found.
N in 100 parts	9·27	9·54

Anilidoacetic acid was also obtained by reducing the acid $C_{11}H_{12}N_2O_3$ with sodium amalgam in aqueous solution. No aniline was formed; but a strong smell of a ketine was perceived. We reduced simultaneously isonitrosoacetone with sodium amalgam and perceived the same smell.

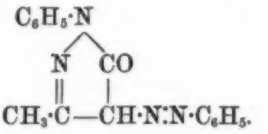
The acid, $CH_3\cdot CO\cdot CH{:}N\cdot N(C_6H_5)\cdot CH_2\cdot COOH$, is therefore broken up by the nascent hydrogen with separation of the nitrogen-atoms, one-half of the molecule yielding anilidoacetic acid, the other a ketine. The formation of anilidoacetic acid from this acid proves that the latter has the constitution here assigned to it, and thus, indirectly, that the so-called "benzene-azo-acetone" is *pyruvaldehydrazone*.

2. *Action of Phenylhydrazine on some Ketonic Compounds containing the Phenylhydrazone-group.*

Action on Ethylic Phenylhydrazone-acetoglyoxylate ("*Benzene-azo-acetoacetate*").—10 grams of ethylic phenylhydrazone-acetoglyoxylate and 5·5 grams of phenylhydrazine were heated with glacial acetic acid in a sealed tube for an hour, at 120—130°. On cooling, the tube

* As the substance here extracted was anilidoacetic acid, we would point out that Schwebel's statement (*Ber.*, **10**, 2046) that this acid is insoluble in ether is incorrect. Michaelson and Lippmann, the discoverers of anilidoacetic acid, say (*Annalen*, **139**, 236): "It is fairly soluble in water, less soluble in ether." This is correct. The statement as to its insolubility in ether has passed into Beilstein's *Handbuch*.

was found to be filled with red needles, with a characteristic blue reflex; these, after crystallisation from glacial acetic acid, melted at 155°. These properties pointed to the identity of the compound with Knorr's (1)-*phenyl*-(3)-*methylpyrazolone*-(4)-*azobenzene* (*Annalen*, **238**, 183), which this author obtained by the action of diazobenzene salts on phenylmethylpyrazolone, and to which he assigns the constitution—



In the present case it is formed according to the equation—

$$CH_3{\cdot}CO{\cdot}\underset{\displaystyle \ddot{N}{\cdot}NHC_6H_5}{C}{\cdot}COOC_2H_5 + C_6H_5{\cdot}NH{\cdot}NH_2 = C_{16}H_{14}N_4O + C_2H_6O + H_2O.$$

A nitrogen determination gave the following result:—

0·0967 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18°, and under 556 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 18°, and under 550 mm. pressure.

	Calculated for $C_{16}H_{14}N_4O$.	Found.
N in 100 parts.....	20·14	20·06

Although ethylic phenylhydrazone-acetoglyoxylate must be regarded as a hydrazone, we should not like positively to affirm the same of the pyrazolone-derivative obtained from it in the foregoing reaction. It is quite conceivable that in the formation of this compound the hydrazone-group is transformed into an azo-group; and, indeed, the extremely pronounced colour of Knorr's compound would rather indicate the occurrence of such a change.*

Action on Phenylhydrazone-acetoglyoxylic Acid.—When phenylhydrazone-acetoglyoxylic acid is warmed with phenylhydrazine in alcoholic solution, *osazone-acetoglyoxylic acid*—

$$CH_3{\cdot}\underset{\displaystyle \underset{\displaystyle COOH}{\dot{C}}:N_2HC_6H_5}{\dot{C}}:N_2HC_6H_5,$$

separates almost immediately in slender, yellow needles, melting at 209°. This acid was obtained by Knorr (*Annalen*, **238**, 195) by the action of phenylhydrazine on rubazonic acid. Knorr gives the melting point at 212°.

* Compare also Bernthsen, *Ber.*, **21**, 743.

0·1048 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15·8° and under 572 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 16° and under 555 mm. pressure.

	Calculated for $C_{16}H_{16}N_4O_2$.	Found.
N in 100 parts	18·92	19·00

When heated with acetic acid, this compound parts with the elements of 1 mol. H_2O, and yields the foregoing phenylmethylpyrazolone-azobenzene, melting at 155°.*

Action on Pyruvaldehydrazone.—Pyruvaldehydrazone and phenylhydrazine, when heated together in alcoholic solution, react, yielding the compound—

$$\begin{matrix} CH_3\cdot C\cdot N_2HC_6H_5 \\ \quad\quad CH\cdot N_2HC_6H_5 \end{matrix}$$

It is deposited from hot alcohol, in which it is only sparingly soluble, as a yellowish crystalline powder, melting at 145°. It dissolves in concentrated sulphuric acid in the cold with an olive-green colour, which speedily changes to slate-blue, and finally, after standing for some hours, to violet. A drop of the blue or violet solution, poured into a porcelain basin and breathed upon, becomes first green, and afterwards yellow.

0·0889 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16·2°, and under 561·5 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 16·5° and under 551 mm. pressure.

	Calculated for $C_{15}H_{16}N_4$.	Found.
N in 100 parts	22·22	22·08

Assuming that the above formula is correct, the compound should be identical with the osazone of pyruvaldehyde (methylglyoxal) obtained by v. Pechmann by the action of phenylhydrazine on pyruvaldehyde and also by heating isonitrosoacetone with phenylhydrazine in acetic acid solution (*Ber.*, **20**, 2543). We therefore prepared the

* After the above was already in type, we received No. 6 of the *Berichte*, 1888, in which Knorr describes the formation of phenylmethylpyrazolone-azobenzene from osazone-acetoglyoxylic acid, and points out its identity with phenylhydrazone-phenylmethylketopyrazolone (*Ber.*, **21**, 1203). Knorr is of opinion that the compound is a hydrazone.

Knorr converts the osazone into the pyrazolone-compound by dissolving it in caustic alkali and precipitating with acetic acid.

compound by the latter method, and found that it agreed in all its properties with that above described.

3. *Action of Diazo-salts on Monalkyl-derivatives of Ethylic Acetoacetate: Formation of Hydrazones of α-Ketonic Acids.*

Ethylic Methacetoacetate and Diazobenzene Chloride.—An aqueous solution of diazobenzene chloride was gradually added in equimolecular proportion to an alcoholic solution of ethylic sodiomethacetoacetate, cooling during the process. The liquid became deep red, and towards the end of the operation a dark-red oil separated. Water was then added to complete the precipitation, after which the oil generally solidified. When this did not occur, the oil was washed with water in a separating funnel and then mixed with alcohol, which caused it to become solid and crystalline. The solid substance was recrystallised several times, first from alcohol, afterwards from light petroleum, by which means it was obtained in yellow needles, melting at 117°.

Analysis led to the formula $C_{11}H_{14}N_2O_2$:—

I. 0·2050 gram gave 0·4820 gram CO_2 and 0·1255 gram H_2O.

II. 0·1123 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of nitrogen, measured dry at 17·6°, and under 438 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{11}H_{14}N_2O_2$.	Found. I.	Found. II.
C	64·08	64·12	—
H	6·80	6·80	—
N	13·59	—	13·70
O	15·53	—	—
	100·00		

The acid was readily obtained by warming the "ester" with an alcoholic solution of caustic soda and precipitating with hydrochloric acid. It crystallises from hot benzene in yellowish needles, melting with evolution of gas at 185°. It dissolves in cold concentrated sulphuric acid with a yellow colour, which soon changes to a deep-red. On allowing a drop of the concentrated red solution to flow about in a porcelain basin, and breathing on it, the colour changes to blue.

Analysis gave figures agreeing with the formula $C_9H_{10}N_2O_2$:—

I. 0·2202 gram gave 0·4893 gram CO_2 and 0·1126 gram H_2O.

II. 0·1101 gram, burnt with oxide of copper in a vacuum, gave 22·63 c.c. of nitrogen, measured dry at 23·4°, and under 501 mm. pressure. Nitric oxide was not present.

	Calculated for $C_9H_{10}N_2O_2$.	Found. I.	Found. II.
C	60·67	60·60	—
H	5·62	5·68	—
N	15·73	—	15·68
O	17·98	—	—
	100·00		

This acid proved, as already mentioned, to be identical with E. Fischer and Jourdan's *phenylhydrazonepyruvic acid*,

$$CH_3\cdot C\cdot COOH$$
$$\ddot{N}\cdot NHC_6H_5,$$

(*Ber.*, **16**, 2241). Fischer and Jourdan give the melting point of their acid at 169°; but, later, Fischer (*Ber.*, **17**, 578) stated that this was a misprint for 192°, which he gives as the true melting point of the acid.* We therefore carefully purified specimens of acid prepared both by our method and by that of Fischer and Jourdan, but in

* In an earlier communication on this subject (*Ber.*, **20**, 3285), we unfortunately overlooked Fischer's correction, and stated that Fischer and Jourdan had given the melting point "much too low." Our attention was called to the oversight by V. Meyer (*Ber.*, **21**, 18). Fischer's correction appears to have escaped notice in another quarter: thus Sandmeyer, in a paper emanating from the laboratory of the Zürich Polytechnic (*Ber.*, **20**, 641), identifies pyruvic acid by means of its phenylhydrazone, which, according to him, "after dissolving once in dilute ammonia and precipitating with hydrochloric acid, showed *the correct melting point of* 169°."

Since the foregoing was written, Professor Fischer has alluded to the subject of the melting point of phenylhydrazonepyruvic acid (*Ber.*, **21**, 987). After pointing out that the acid, as a substance which decomposes in melting, will show too low a melting point unless rapidly heated, he adds:—"It was evidently from this cause that Messrs. Japp and Klingemann, who have overlooked both my corrected statement as to the melting point" [*i.e.*, that 169° was a misprint for 192°], "and my remarks on the mode of heating, found the melting point of the compound first at 182° and afterwards at 185°."

There is a point here which calls for correction. We stated (*Ber.*, **20**, 3285) that, in our first communication, the melting point of the compound "was erroneously given at 182°, instead of at 185°." Professor Fischer somewhat hastily concludes that "erroneously *given*" is synonymous with "erroneously *found*." As a matter of fact, the error in question was an error in transcribing, although we did not specify this at the time, imagining that the cause of such an error—whether a misprint, as in Professor Fischer's case, or otherwise—could be of interest to no one save the authors.

We have already expressed our regret that we overlooked Professor Fischer's correction. As regards the other oversight—of Professor Fischer's "remarks on the mode of heating"—we would point out that we expressly stated that the compound decomposed in melting, and we are under the impression that the precaution to be taken in determining the melting point of substances of this character was

neither case could we succeed in raising the melting point above 185°, which we must therefore regard as the correct melting point.

Both acids, on heating, yielded a crystalline compound of the formula $C_{16}H_{18}N_4$—diacetylosazone (*vide supra*)—together with oily matters.

We also found that Fischer and Jourdan's acid gave the above characteristic colour reaction with concentrated sulphuric acid.

Fischer and Jourdan give the melting point of the ethyl salt of their acid at 114—115°. We found, for the ethyl salt prepared as above described, the melting point 117°.

The metallic salts appear to be very unstable, and could not be obtained in a state fit for analysis.

We reduced the acid obtained by the above method with sodium amalgam. By moderate reduction of the sodium salt in aqueous solution with sodium amalgam, a hydrazo-acid was obtained, which was precipitated on acidifying with hydrochloric acid, avoiding an excess, which was found to redissolve the hydrazo-acid. It crystallised from methyl alcohol in slender, colourless needles, which on exposure to air become yellow, especially when moist. We found the melting point at 170°, but had not sufficient substance for further recrystallisation; the true melting point is 172°* (see later on). The substance evolves gas in melting. Analysis gave figures agreeing with the formula $C_9H_{12}N_2O_2$:—

I. 0·1910 gram gave 0·4207 gram CO_2 and 0·1174 gram H_2O.

II. 0·0978 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16·8° and under 435 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 16·9° and under 430 mm. pressure.

	Calculated for $C_9H_{12}N_2O_2$.	Found. I.	Found. II.
C	60·00	60·07	—
H	6·67	6·83	—
N	15·55	—	15·58
O	17·78	—	—
	100·00		

known before Professor Fischer illustrated it in the case of the hydrazones. We made a point of heating as rapidly as is practicable.

Professor Fischer's explanation will hardly account for the fact that in the case of the corresponding hydrazo-acid—also a compound which decomposes in melting—we found the melting point 20° *higher* than he did.

* The melting point (162°) given in our first publication on this subject (*Ber.*, 20, 2943) is too low. The substance had not been sufficiently purified.

This acid would be *benzene-α-hydrazopropionic acid*,

$$\begin{matrix} CH_3\cdot CH\cdot COOH \\ \quad\quad NH\cdot NHC_6H_5 \end{matrix}$$

Fischer and Jourdan (*Ber.*, **16**, 2244) obtained this acid by the reduction of phenylhydrazonepyruvic acid, but assign to it the melting point 152—154°. We therefore prepared phenylhyrazonepyruvic acid from phenylhydrazine and pyruvic acid, and reduced it with sodium amalgam. The hydrazo-acid thus obtained was identical with the foregoing, and after repeated recrystallisation from methyl alcohol had a constant melting point of 172°.

Aniline is always formed in this reduction, as observed by Fischer and Jourdan. We therefore endeavoured to isolate the other product which would be formed by the breaking up of the molecule of the hydrazo-acid by reduction—alanine. A quantity of phenylhydrazonepyruvic acid was dissolved in dilute caustic soda and treated with excess of sodium amalgam on the water-bath. The aniline which was formed was then extracted with ether; the alkaline aqueous solution was slightly acidified with hydrochloric acid, thus precipitating a small quantity of the hydrazo-acid, which was removed by filtration; the filtrate was evaporated to dryness, and the residue treated with boiling absolute alcohol to extract the alanine hydrochloride, which remained as a crystalline residue on evaporating the alcohol; this residue was boiled with water and litharge; the filtered solution, containing the lead salt of alanine, was precipitated with sulphuretted hydrogen; and the filtrate from the lead sulphide was evaporated to a small bulk and then mixed with an excess of alcohol. Alanine separated in slender white needles. The alanine thus obtained had a sweet taste; sublimed above 200°, and gave on analysis :—

	C.	H.	N.	
Calculated for $C_3H_7NO_2$..	40·45	7·86	15·73	per cent.
Found	40·38	8·03	15·61	„

Ethylic Methacetoacetate and o-Diazotoluene Chloride.—The reaction was conducted as in the former case. The "ester" was obtained as a red oil which did not solidify, even in a freezing mixture: it was therefore hydrolysed by heating with caustic soda and alcohol. The acid was precipitated with hydrochloric acid and purified by recrystallisation from benzene. It formed small yellowish laminæ, melting, with evolution of gas, at 156°. It is identical with Raschen's *o-tolylhydrazonepyruvic acid* (*Annalen*, **239**, 228), which we prepared from pyruvic acid and *o*-tolylhydrazine hydrochloride for the purpose of comparing it with our compound. Raschen gives

the melting-point at 158—159°. The acid prepared by our method gave the following figures on analysis:—

I. 0·2214 gram gave 0·5051 gram CO_2 and 0·1221 gram H_2O.

II. 0·0988 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15·7° and under 412 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. dry nitrogen at 16° and under 408 mm. pressure.

	Calculated for $C_{10}H_{12}N_2O_2$.	Found. I.	Found. II.
C	62·50	62·22	—
H	6·25	6·13	—
N	14·58	—	14·67
O	16·67	—	—
	100·00		

The hydrazo-acid, which had not hitherto been prepared, was obtained by reducing the acid from *o*-diazotoluene and ethylic methacetoacetate with sodium amalgam. The acid was precipitated by careful addition of hydrochloric acid and recrystallised from methyl alcohol. It formed tufts of small, colourless needles, melting at 143°. This melting point is possibly too low, as the quantity of substance was insufficient for further recrystallisation.

	Substance.	CO_2.	H_2O.
I.....	0·1911	0·4306	0·1262
II.....	0·2048	0·4617	0·1331

III. 0·0998 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of nitrogen, measured dry at 20° and under 412 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{10}H_{14}N_2O_2$.	Found. I.	Found. II.	Found. III.
C	61·86	61·45	61·48	—
H	7·22	7·33	7·22	—
N	14·43	—	—	14·39
O	16·49	—	—	—
	100·000			

The acid is consequently the expected *o-toluenehydrazopropionic acid*,

$$CH_3{\cdot}\dot{C}H{\cdot}COOH$$
$$\dot{N}H{\cdot}NHC_6H_4{\cdot}CH_3(1, 2).$$

o-Toluidine was regenerated during the reduction.

Ethylic Methacetoacetate and p-Diazotoluene Chloride.—In this case, the "ester," when precipitated with water, solidified. It was deposited in yellowish laminæ from light petroleum, and in needles from alcohol, melting at 106°.

	C.	H.	N.	
Calculated for $C_{12}H_{16}N_2O_2$ ..	65·45	7·27	12·73	per cent.
Found	65·64	7·33	13·05	„

The "ester" was hydrolysed with alcoholic caustic soda. The precipitated acid was recrystallised from benzene, from which it was deposited in yellow laminæ melting at 162° with evolution of gas

	C.	H.	N.	
Calculated for $C_{10}H_{12}N_2O_2$ ..	62·50	6·25	14·58	per cent.
Found	62·48	6·28	14·54	„

This acid is identical with Raschen's *p-tolylhydrazonepyruvic acid* (*Annalen*, **239**, 224), which we prepared for comparison. Raschen gives the melting point of the acid at 158—160°; that of the ethyl salt at 106—107°.

The hydrazo-acid was not prepared.

Ethylic Ethacetoacetate and Diazobenzene Chloride.—In this case, diazobenzene chloride was added to the molecular proportion of ethylic sodethacetoacetate dissolved in alcohol. The new "ester," when precipitated with water, did not solidify, and was therefore hydrolysed with alkali. The acid, precipitated with hydrochloric acid, was purified by recrystallisation from benzene, which deposited it in yellow needles, with a silky lustre, melting with decomposition at 152°.

I. 0·1984 gram gave 0·4543 gram CO_2 and 0·1139 gram H_2O.

II. 0·0927 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of nitrogen, measured dry at 16° and under 384 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{10}H_{12}N_2O_2$.	Found. I.	Found. II.
C	62·50	62·44	—
H	6·25	6·37	—
N	14·58	—	14·63
O	16·67	—	—
	100·00		

The acid is *phenylhydrazonepropionylformic acid*,

$$CH_3{\cdot}CH_2{\cdot}C{\cdot}COOH$$
$$\ddot{N}{\cdot}NHC_6H_5$$

In the preliminary account of these reactions which we published (*Ber.*, **20**, 2943), we described this acid, regarding it, however, as "benzene-α-azobutyric acid." Later, W. Wislicenus and E. Arnold (*Ber.*, **20**, 3395) described an acid obtained from propionylformic acid and phenylhydrazine, which ought to be identical with the foregoing. They state that it crystallises from dilute alcohol in laminæ melting at 144—145°.

By reduction of the sodium salt of the above acid in aqueous solution with sodium amalgam, *benzene-α-hydrazobutyric acid*,

$$CH_3 \cdot CH_2 \cdot \underset{NH \cdot NH_6H_5}{\overset{}{C}}H \cdot COOH$$

was obtained. The hydrazo-acid, precipitated by hydrochloric acid, avoiding an excess, and recrystallised from methyl alcohol, formed small colourless needles. The compound exhibits a peculiar behaviour on heating. At 165°, it softens, without distinctly melting, and a substance which colours the sulphuric acid in the melting-point bulb violet distils out of the capillary tube; then the contents of the tube again become solid; and before the temperature of 245° is reached, at which a slight residue still left in the capillary tube melts, nearly everything has sublimed out of the tube. The substance was dried over sulphuric acid for analysis.

	Substance.	CO_2.	H_2O.
I	0·2098	0·4763	0·1395
II	0·2047	0·4645	0·1337

III. 0·0970 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitrous oxide, measured dry at 20° and under 406 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 20°, and under 402 mm. pressure:—

	Calculated for $C_{10}H_{14}N_2O_2$.	Found.		
		I.	II.	III.
C	61·86	61·91	61·88	—
H	7·22	7·39	7·25	—
N	14·43	—	—	14·51
O	16·49	—	—	—
	100·00			

4. *Action of Diazo-salts on Ketonic Acids: Formation of Monohydrazones of α-Dicarbonyl-compounds.*

Acetoacetic Acid and Diazobenzene Chloride.—65 grams of ethylic acetoacetate were dissolved in a solution of 30 grams of caustic

potash in 1120 grams of water, and allowed to stand for 24 hours, after which the solution was acidified with hydrochloric acid in order to liberate the acetoacetic acid. A solution of the molecular proportion of diazobenzene chloride (from 47 grams of aniline and 35 grams of sodium nitrite), *containing a slight excess of hydrochloric acid*, was then added. The acid solutions remain clear when first mixed; then a separation of pyruvaldehydrazone ("benzene-azo-acetone"), $CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$, commences, accompanied by an evolution of carbon dioxide; but the reaction takes place very slowly, and is not quite complete even at the end of eight hours. It is therefore better to add to the acid solution, after mixing, an excess of a solution of sodium acetate; the reaction then takes place rapidly, and an almost quantitative yield of a practically pure product is obtained. In both cases, the pyruvaldehydrazone separates in a crystalline form. It is probably advisable to use rather less diazo-salt than the theory requires.

After recrystallising twice from benzene, the pyruvaldehydrazone showed the proper melting point, 149—150°. It yielded a phenylhydrazine-derivative melting at 145°, which gave with concentrated sulphuric acid the characteristic colour reaction (p. 531).

The above is, both as regards yield and purity of the product, by far the best method as yet known of preparing pyruvaldehydrazone.

Methacetoacetic Acid and Diazobenzene Chloride.—The operation was conducted as in the foregoing experiment, substituting 72 grams of ethylic methacetoacetate for the ethylic acetoacetate. On adding sodium acetate to the hydrochloric acid solution of methacetoacetic acid and diazobenzene chloride, *diacetylhydrazone*,

$$\begin{matrix} CH_3{\cdot}C{:}N{\cdot}NHC_6H_5 \\ CH_3{\cdot}CO \end{matrix},$$

separated in minute needles with evolution of carbon dioxide. The crude product was treated with sodium carbonate to remove any phenylhydrazonepyruvic acid that might have been formed from unhydrolysed ethylic methacetoacetate, and then recrystallised from hot benzene, which deposited it in yellow, tabular crystals, mostly grouped staircase-fashion, melting at 133°.

0·2350 gram gave 0·5847 gram CO_2 and 0·1414 gram H_2O.

	Calculated for $C_{10}H_{12}N_2O$.	Found.
C	68·18	67·85 per cent.
H	6·82	6·68 „

The monophenylhydrazone of diacetyl has been prepared from diacetyl and phenylhydrazine by v. Pechmann (*Ber.*, **20**, 3164), who

gives the melting point at 133°, with which our determination exactly agrees.

On pouring a concentrated aqueous solution of phenylhydrazine hydrochloride into a hot alcoholic solution of the above monohydrazone, the *osazone*, $\begin{matrix}CH_3\cdot C\cdot N\cdot NH\cdot C_6H_5\\ CH_3\cdot C\cdot N\cdot NH\cdot C_6H_5,\end{matrix}$ separates as a yellow crystalline powder melting at 243°. v. Pechmann (*loc. cit.*) gives 242° as the melting point of diacetylosazone, which we also prepared from diacetyl and phenylhydrazine, and found identical in all its properties with the compound obtained by us. A nitrogen determination was made with our compound:—

0·1074 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 11° and under 627 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 11° and under 621 mm. pressure.

	Calculated for $C_{16}H_{18}N_4$.	Found.
N in 100 parts	21·05	20·88

Diacetylosazone gives a colour-reaction with concentrated sulphuric acid. It dissolves in the cold with a brown colour; but this speedily changes to a claret-red, which in thin layers appears green.

Ethacetoacetic Acid and Diazobenzene Chloride.—The experiment was performed as in the preceding cases, except that the ethylic ethacetoacetate required longer shaking with the caustic potash solution to make it dissolve, and owing to the greater difficulty with which it is hydrolysed, it was allowed to stand in alkaline solution for 48 hours instead of for 24. In this case, the propionylacetylhydrazone $\begin{matrix}C_2H_5\cdot C\cdot N\cdot NHC_6H_5\\ CH_3\cdot CO\end{matrix}$, separated as a red oil on the addition of sodium acetate to the hydrochloric acid solution of ethacetoacetic acid and diazobenzene chloride. On dissolving this oil in a small quantity of alcohol, the new compound was deposited in a solid form. The product was treated with sodium carbonate to remove any acid. From concentrated solutions in hot benzene, it crystallised in yellow needles or prisms radiating from a point; from dilute solutions, in large, transparent plates. It melted at 116—117°.

In spite of the apparent purity of the substance, the carbon was found to be 1 per cent. too low on analysis, and the hydrogen was also too low. Only after repeated recrystallisation from benzene were numbers obtained agreeing fairly well with the theory:—

	Substance.	CO_2.	H_2O.
I	0·2669	0·6762	0·1748
II	0·2333	0·5908	0·1506

	Calculated for $C_{11}H_{14}N_2O$.	Found. I.	Found. II.
C	69·47	69·09	69·06
H	7·36	7·28	7·17

Even in these analyses, the hydrogen is too low. We suspect, therefore, that the substance was contaminated with a small quantity of pyruvaldehydrazone, which would be formed if the ethylic ethacetoacetate contained, as it very easily might, unchanged ethylic acetoacetate. We find that propionylacetylhydrazone and pyruvaldehydrazone crystallise together.

Possibly a small quantity of the same impurity, formed in the same way, was present in the specimen of diacetylhydrazone which we analysed (*ante*), in which the hydrogen was also found too low.

The *osazone* of propionylacetyl, $\begin{matrix}C_2H_5\cdot C\cdot N\cdot NHC_6H_5\\ CH_3\cdot C\cdot N\cdot NHC_6H_5,\end{matrix}$ was obtained by heating an alcoholic solution of the foregoing compound with phenylhydrazine hydrochloride and sodium acetate. It crystallises from benzene in yellow needles melting at 162°, which give with concentrated sulphuric acid exactly the same colour-reaction as the osazone of diacetyl (p. 540).*

0·1012 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide measured dry at 14° and under 557 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 14° and under 553 mm. pressure.

	Calculated for $C_{17}H_{20}N_4$.	Found.
N in 100 parts	20·00	19·51

5. *Action of Heat on Hydrazones of Ketonic Acids and on Aldehydrazones: Formation of Osazones.*

Action of Heat on Phenylhydrazonepyruvic Acid.—A quantity of phenylhydrazonepyruvic acid was heated in an oil-bath at 180—190° until gas ceased to be evolved. From the dark-coloured oil thus obtained, a crystalline substance separated on adding alcohol. It was

* No. 6 of the *Berichte*, received after the above was in type, contains an account of the hydrazones of propionylacetyl by v. Pechmann. The author prepared these compounds by the direct action of phenylhydrazine on propionylacetyl. He finds that the monohydrazone obtained in this way is distinct from our compound, and he therefore assigns to it the formula—

$$\begin{matrix}C_2H_5\cdot CO\\ CH_3\cdot C\cdot N\cdot NHC_6H_5\end{matrix}$$

For the osazone he finds the melting point at 161—162·5°, agreeing with our determination.

washed with hot alcohol, in which it is only sparingly soluble, and dried for analysis. It formed a yellow crystalline powder, melting at 238°. Analysis led to the formula $C_{16}H_{18}N_4$.

I. 0·1717 gram gave 0·4536 gram CO_2 and 0·1041 gram H_2O.

II. 0·1047 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14·7° and under 617 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 15° and under 610 mm. pressure.

	Calculated for $C_{16}H_{18}N_4$.	Found. I.	Found. II.
C	72·18	72·04	—
H	6·77	6·73	—
N	21·05	—	20·78
	100·00		

The compound was soluble in cold concentrated sulphuric acid with a brown colour, changing afterwards to a claret-red, which in thin layers appeared green.

The formula and the colour-reaction with sulphuric acid are therefore those of *diacetylosazone* (p. 540), with which the compound is indeed identical. The difference in the melting point—238° instead of 242°—is due to the fact that the substance, owing to the smallness of the quantity available, was not recrystallised. The yield is very small.

The formation of the osazone of diacetyl in the above reaction may be expressed thus:—

$$\begin{array}{l} CH_3\cdot C{:}N_2HC_6H_5 \\ \quad | \\ \quad COOH \\ \quad COOH \\ \quad | \\ CH_3\cdot C{:}N_2HC_6H_5 \end{array} = \begin{array}{l} CH_3\cdot C{:}N_2HC_6H_5 \\ CH_3\cdot C{:}N_2HC_6H_5 \end{array} + 2CO_2 + H_2.$$

Action of Heat on Aldehydrazone.—As already mentioned, Fischer and Jourdan have shown (*loc. cit.*) that the oil which is obtained on heating phenylhydrazonepyruvic acid mainly consists of aldehydrazone (ethylidenephenylhydrazine)—

$$\begin{array}{l} CH_3\cdot C{:}N_2HC_6H_5 \\ \quad COOH \end{array} = CH_3\cdot CH{:}N_2H\cdot C_6H_5 + CO_2.$$

It therefore seemed possible that the osazone of diacetyl had been formed from the aldehydrazone in a secondary reaction according to the equation—

$$2CH_3{\cdot}CH{:}N_2HC_6H_5 = \begin{matrix}CH_3{\cdot}C{:}N_2HC_6H_5\\ CH_3{\cdot}C{:}N_2HC_6H_5\end{matrix} + H_2.$$

We therefore heated aldehydrazone with a reflux condensing-tube for three hours. On adding alcohol to the liquid product, the expected osazone separated as a crystalline powder. It was identified by its melting point (237—238°) and by the reaction with sulphuric acid. The yield is very small, but may be somewhat increased by passing air through the aldehydrazone during the heating process.

The osazone obtained by the above methods was carefully compared with a specimen prepared from diacetyl and phenylhydrazine.

Action of Heat on the Tolylhydrazonepyruvic Acids.—*o*-Tolylhydrazonepyruvic acid, when heated for some time at its melting point, yielded in like manner *diacetyl-o-tolylosazone*,

$$\begin{matrix}CH_3{\cdot}C{:}N_2H{\cdot}C_6H_4{\cdot}CH_3\\ CH_3{\cdot}C{:}N_2H{\cdot}C_6H_4{\cdot}CH_3\end{matrix}\ (1, 2),$$

which separated from the oily product of the reaction on adding alcohol. It formed a yellow crystalline powder melting at 198°, sparingly soluble in alcohol. The sulphuric acid reaction is not characteristic; the compound dissolves in the concentrated acid with a brown colour which afterwards changes to a reddish-brown.

The same compound was obtained by heating an aqueous solution of diacetyl with *o*-tolylhydrazine hydrochloride and sodium acetate.

I. 0·0827 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15·5° and under 448 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 15·5° and under 444 mm. pressure.

II. 0·0754 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14° and under 402 mm. pressure. After absorption of nitric oxide, there remained 22·63 c.c. of dry nitrogen at 14° and under 400 mm. pressure.

	Calculated for $C_{18}H_{22}N_4$.	Found. I.	Found. II.
N in 100 parts	19·05	19·08	18·92

Analysis I was made with a preparation obtained from *o*-tolylhydrazonepyruvic acid; analysis II with a preparation from diacetyl and *o*-tolylhydrazine.

p-Tolylhydrazonepyruvic acid yields, when heated, *diacetyl-p-tolylosazone*, $\begin{matrix}CH_3{\cdot}C{:}N_2H{\cdot}C_6H_4{\cdot}CH_3\\ CH_3{\cdot}C{:}N_2H{\cdot}C_6H_4{\cdot}CH_3\end{matrix}$ (1, 4). It was separated like the foregoing compounds of this class, and formed a yellow, crystalline powder

melting at 229—230°. It dissolves in cold concentrated sulphuric acid with a brown colour, which changes, through yellow and greenish-yellow, to green.

0·1101 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 11° and under 585 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 11° and under 580 mm. pressure.

	Calculated for $C_{18}H_{22}N_4$.	Found.
N in 100 parts	19·05	19·02

The same compound was obtained by the action of *free* *p*-tolylhydrazine on diacetyl in ethereal solution. Curiously enough, when we attempted to prepare the compound, like its ortho-isomeride, by heating an aqueous solution of diacetyl with *p*-tolylhydrazine hydrochloride and sodium acetate, only the *mono-p-tolylhydrazone*, $CH_3{\cdot}C(:N_2H{\cdot}C_6H_4{\cdot}CH_3)(1,4)$, $CH_3{\cdot}CO$ was formed. It crystallises from benzene in slender yellow needles melting at 161°. A nitrogen determination gave 14·91 per cent. Calculated: N 14·73 per cent.

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XL.—*The Influence of Temperature on the Composition and Solubility of Hydrated Calcium Sulphate and of Calcium Hydroxide.*

By W. A. Shenstone and J. Tudor Cundall.

I. Such facts as the extraordinary solubility of silver nitrate at temperatures above 100°,* and the evidence of a distinct relation between the solubility of salts at high temperatures and their melting points,* together with the circumstance that high temperature, though favourable to dissociation, diminishes the solubility of only a few substances, are apparently inconsistent with the idea that in all cases the solubility of salts in water is due to the formation of definite hydrates. Yet, on the other hand, even before the recent publications of Mendeléeff and others, there was considerable reason for supposing that in many cases the solubility of anhydrous salts in water is

* Tilden and Shenstone, *Phil. Trans.*, 1884, Part I.

accompanied by and influenced by the formation of such hydrates.* And it has been supposed that the influence of high temperature in reducing the solubility of several salts, is due to dissociation of soluble hydrated compounds, the products of the dissociation in these cases being less soluble than the compounds from which they have been formed. This view receives some support from the fact that several of the salts in question, for instance, sodium sulphate and copper sulphate, form well-known hydrates which are readily decomposed on heating even in the presence of a large excess of water.† On the other hand, however, in the case of some others, such as sulphate of calcium, the only known hydrates have been supposed to be comparatively stable even in dry air. As a satisfactory theory of solution must be wide enough to include an explanation of the peculiar behaviour of these salts, we have thought it worth while to spend some time on the experiments described in this paper, and we think that our results will be found to be a useful contribution to this side of the "solution question," although in the case of calcium hydroxide they are at present partly of a negative character.

II. *The Influence of Temperature on Hydrated Calcium Sulphate.*—The statements on this subject in works on chemistry vary considerably, but all agree so far, that they lead to the conclusion that a temperature above 100° is necessary to start the dehydration of the salt, and that a considerably higher temperature is required for its complete desiccation. For example, Hannay (*J. Chem. Soc.*, 1887, ii, 381) states that in dry air, dehydration of calcium sulphate does not commence till a temperature of 118° is reached, but that subsequently it proceeds at as low a temperature as 100° (Bar. = 760 mm.), until 15 per cent. of water has been expelled.

Our results do not agree very well with any of these statements; for in consequence of conducting our experiments with the special view of detecting small changes (viz., by employing a set of weights whose exact relations were known, and by resorting to the method of vibrations in weighing), we observed, at an early stage, a peculiarity in the behaviour of the substance that has previously been overlooked.

Experiment I.—A known mass of pure hydrated calcium sulphate of our own preparation was placed in a flask, A, and, after the removal of hygroscopic moisture by means of a current of dry air, was heated in a slow current of air which had been dried by means of phosphorus

* It is not unlikely that in some cases, for instance in that of calcium sulphate, solubility depends entirely on the existence of one or more hydrated compounds.

† We find this to be true in the case of $CuSO_4,5H_2O$ at temperatures above 100°.

pentoxide, until its weight became constant at 70°, 100°, and 150°. A similar experiment was made on a portion of powdered selenite.

In these experiments the admission of moisture to the contents of A during cooling and weighing was prevented by means of well-fitting stoppers, B, C, and the two tubes were securely plugged with glass-wool to prevent the mechanical conveyance of particles of salt from A by the current of air. We assured ourselves of the efficiency of these precautions by repeated experiments.

As hot water attacks glass vessels in the prolonged exposure necessary in these experiments to an extent sufficient to interfere with the accuracy of the work, and as paraffin is inconvenient to work with, A was plunged into a copper-bath filled with shot, the copper-bath being itself placed in a vessel containing water or paraffin. The temperature of A was determined by means of a thermometer whose bulb was immersed in the shot and in contact with A.

TABLE I.—*Showing the Results of Experiment I.*

Temperature.	Total loss per cent. by artificial $CaSO_4,2H_2O$.	Total loss per cent by selenite.
70° C.....	20·67	19·99
100° C.....	20·89	—
150° C.....	21·07	20·45
Low red heat.....	—	20·67

The formula $CaSO_4,2H_2O$ requires 20·9 per cent. of water. It has frequently been observed by others that the total loss of water in drying this salt slightly exceeds that required by theory.

The temperature 70° was selected as the starting point in this experiment, because whilst that temperature is not too far below 100°, the solubility of calcium sulphate at 70° is distinctly lower than at 35°, which is probably the temperature of maximum solubility.

Experiment II.—This experiment was made at 40°, which is only slightly above the temperature of maximum solubility of calcium sulphate. The results obtained are given in Table II. The same method as that described above was employed.

TABLE II.

Time.	Water lost by 2·0460 gram of calcium sulphate at 40°.
6 hours	0·0008 gram
30 „	0·0068 „
48 „	0·0202 „
72 „	0·0308 „
96 „	0·0376 „
120 „	0·0492 „
144 „	0·0600 „

The loss in this case at the end of 144 hours amounted to about 3 per cent., but the change was not yet complete.

Experiment III.—The above experiments seem to establish that, contrary to previous statements, hydrated calcium sulphate parts with the greater part of its water of crystallisation at 70° in dry air, and that even at as low a temperature as 40° it is not absolutely permanent. Whilst we were making them, we were led to think that the results of a careful examination of the rate of loss in equal periods of time would be interesting. Another experiment was therefore made at 70°, in which powdered selenite was heated in A during periods of three hours in a current of dry air which was passed through the apparatus at an average rate of 111·6 c.c. per minute. The results of this experiment, which are given in Table III and curve No. I (p. 550), show that not only is the rate at which this salt dissociates a slow one, but that it is much slower in its earlier stages than afterwards.* We think that these two facts and especially the latter, help to account for the divergent statements that have been made on this subject.

* At higher temperatures the three-hour intervals between the weighings are too long to permit of the detection of this peculiarity in the behaviour of calcium sulphate.

Owing to the fact that most salts part with their water of crystallisation as rapidly during the earlier stages as afterwards (or even more rapidly), chemists frequently neglect slight changes in experiments of this kind. Thus in his careful experiments Hannay heated calcium sulphate for periods of 20 minutes only to the following temperatures: 100°, 103°, 105°, 110°, 115°, and finding no perceptible loss till 118° was reached, concluded that lower temperatures than this were without effect on it.

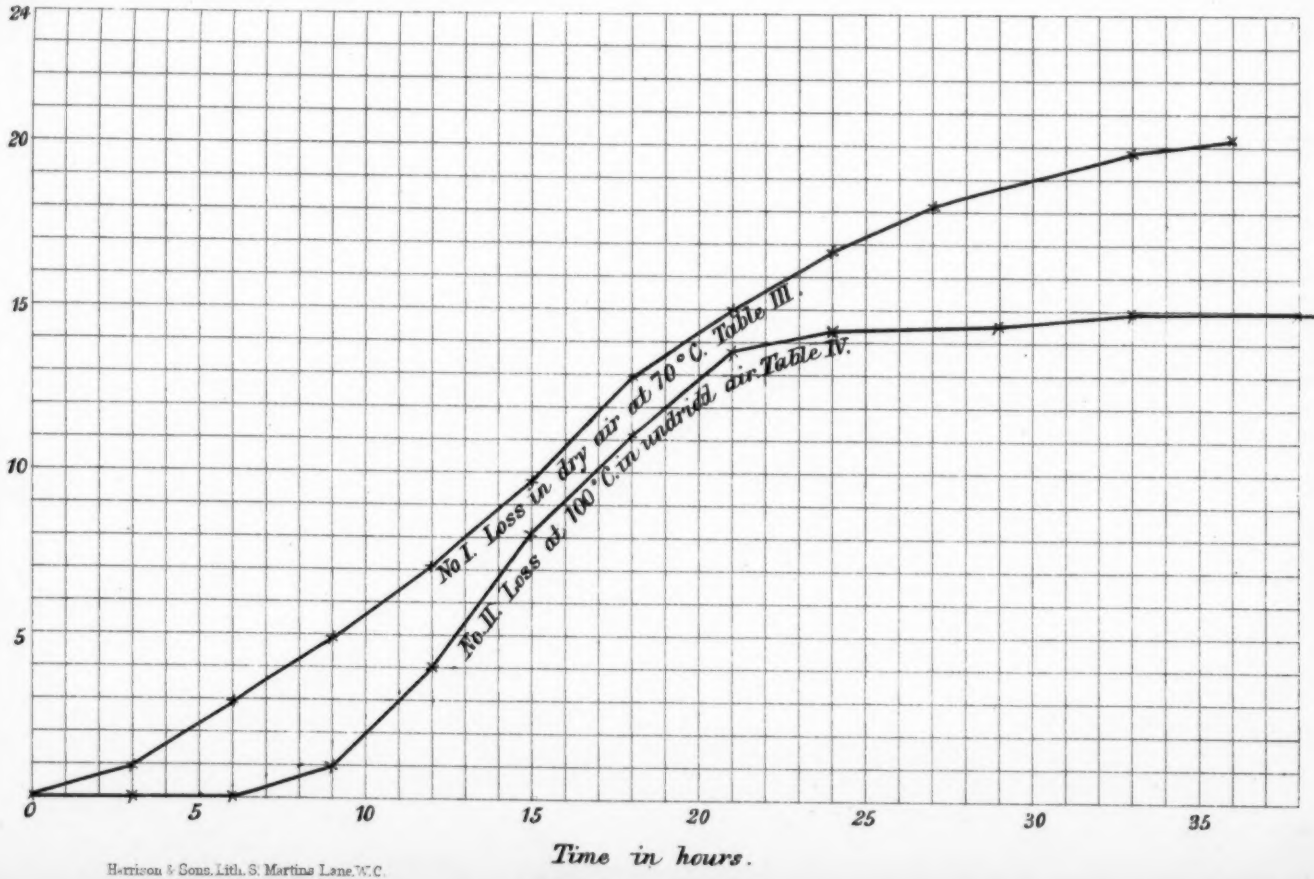
TABLE III (*Curve No.* 1).

Time.	Loss of water in dry air at 70°.
3 hours	0·94 per cent.
6 „	2·86 „
9 „	4·87 „
12 „	7·25 „
15 „	9·73 „
18 „	12·87 „
21 „	14·94 „
24 „	16·72 „
27 „	18·20 „
30 „	19·14 „
33 „	19·87 „
36 „	20·14 „

Experiment IV.—This experiment shows even more markedly the slowness with which calcium sulphate responds to the influence of heat. Table IV gives the results obtained by heating a specimen of powdered selenite at 100° in a water-oven during periods of three hours each. Only a very slow current of undried air was allowed to pass through the oven during the experiment.

TABLE IV (*Curve No.* 2).

Loss of water after		3	hours'	heating	was	0·04 per cent.
„	„	6	„	„	0·075	„
„	„	9	„	„	0·85	„
„	„	12	„	„	4·06	„
„	„	15	„	„	8·30	„
„	„	18	„	„	11·25	„
„	„	21	„	„	13·86	„
„	„	24	„	„	14·69	„
„	„	29	„	„	14·73	„
„	„	33	„	„	14·93	„
„	„	39	„	„	14·93	„



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Experiment V.—The divergent results to which we have alluded are, however, partly to be attributed to the circumstance that different specimens of calcium sulphate ($CaSO_4,2H_2O$) do not behave in exactly the same manner when submitted to identical treatment. Table V gives the results of exposing three different specimens of hydrated calcium sulphate to a temperature of 100° simultaneously under absolutely identical conditions.

In respect to the total loss in undried air, it will be observed that these results agree with those of other observers as well as could be expected under somewhat variable conditions.

Loss of Water per cent. at 100°.

Time.	Artificial $CaSO_4,2H_2O$.	Selenite. T.	Selenite, M.
2 hours.....	4·3	1·3	1·0
4 „	15·0	7·8	5·8
6 „	15·8	11·5	10·0
8 „	15·8	13·8	12·8

Summary.—The results we have obtained show that both in dry and moist air, hydrated calcium sulphate is less stable than has been supposed. Its peculiar behaviour under the influence of heat,* suggests the idea that in the case of this substance we have to deal with molecular aggregates of great stability, and that it is only after the gradual breaking up of these that dissociation can take place.

It will not perhaps be unreasonable in future to place calcium sulphate with those salts whose diminished solubility in hot water may possibly be due to dissociation of definite hydrates. It is true that calcium sulphate is thrown down from a hot solution at a much more rapid rate than that at which dehydration occurs, even in perfectly dry air, at similar temperatures. But if there be any truth in the above suggested explanation of the slow rate at which the solid salt dissociates, this circumstance is of less importance, since it is not unlikely that in the liquid state there is a comparatively simple state of affairs in regard to molecular aggregation, and moreover, the liquid condition is more favourable to the rapid progress of change than the solid state.

It will be noticed that the curves fail to afford any support to the idea that other hydrates of calcium sulphate exist besides that to which we give the formula $CaSO_4,2H_2O$.

* Zinc sulphate behaves in a somewhat similar manner. See Hannay, *loc. cit.*

IV.—*Influence of Temperature on the Composition and Solubility of Calcium Hydroxide.*

Our experiments with this substance are much fewer than in the case of calcium sulphate. A specimen of pure calcium hydroxide, dried at 16° in air free from carbon dioxide, lost only 0·3 per cent. of moisture after prolonged heating to temperatures ranging from 70° to 150° in a current of air thoroughly dried by means of phosphorus pentoxide. This led us to doubt the accuracy of the statements that have been made as to its solubility in hot water, especially as all experiments on the subject, so far as we are aware, have been made in vessels of glass, which might possibly be attacked by the hydroxide as it is at high temperatures by calcium sulphate (Tilden and Shenstone, *loc. cit.*). An experiment was therefore made to test this point.

This experiment was made with the platinum tube employed for similar work by one of us in conjunction with W. A. Tilden in 1885 (*Proc. Roy. Soc.*, vol. 38, p. 331). The utmost care was taken, and a carefully prepared specimen of the hydroxide was employed. We found that at 150°, 3081 parts of solution contained only one part of calcium hydroxide. At 19°, one part of hydroxide was found to be present in 640 parts of solution. No doubt, therefore, remains on this point; calcium hydroxide is very decidedly less soluble in hot water than in cold, but we have at present no information as to the cause of its diminished solubility.

XLI.—*The Action of Phenylhydrazine on Urea and some of its Derivatives.*

By Sidney Skinner, B.A., and S. Ruhemann, Ph.D.

In this paper we give an account of the action of phenylhydrazine on certain compounds nearly related to urea. In the first part, several substances are described, which complete the series of semicarbazides and carbazides both of oxy- and thio-carbamides. The difference between the carbamides and these substances which contain groups of two atoms of nitrogen united directly, is shown by the fact that the latter yield coloured compounds when treated with a mild oxidising agent such as copper sulphate or mercuric chloride.

The latter part of the paper is devoted to a description of the

reaction of phenylhydrazine with parabanic acid, and the comparison of this reaction with that which takes place with alloxan under like conditions. In the cold, phenylhydrazine behaves as ammonia does with parabanic acid, forming the corresponding normal salt, but on boiling with water a hydrazide of oxaluric acid is produced. This reaction is not analogous to that with ammonia at the temperature of boiling water, as that is said to produce the ammonium salt of oxaluric acid.

Diphenylcarbazide.

When a mixture of 2 mols. of phenylhydrazine and 1 mol. of ethylic carbamate is heated over a small flame until the evolution of ammonia ceases, a viscous brown product remains, which crystallises after some days; crystallisation may, however, be at once brought about by adding excess of ether. This compound, diphenylcarbazide, is insoluble in ether, sparingly soluble in hot water, easily in hot alcohol, and is best recrystallised from dilute alcohol. It melts at 151°, and gives a deep red coloration with ammonia.

The formula $CO(NH{\cdot}NH{\cdot}C_6H_5)_2$ requires the following values:—

	Theory.		Found. I.	Found. II.
C_{13}	156	64·46 p. c.	64·02	—
H_{14}	14	5·80 „	6·43	—
N_4	56	23·14 „	—	22·92
O	16	6·60 „	—	—

Its formation takes place in the following way:—

$$CO{<}\begin{matrix}NH_2\\OC_2H_5\end{matrix} + \begin{matrix}NH_2{\cdot}NH{\cdot}C_6H_5\\NH_2{\cdot}NH{\cdot}C_6H_5\end{matrix} = CO{<}\begin{matrix}NH{\cdot}NH{\cdot}C_6H_5\\NH{\cdot}NH{\cdot}C_6H_5\end{matrix} + NH_3 + C_2H_5{\cdot}OH.$$

If the ethereal solution from which the diphenylcarbazide has separated is allowed to stand, other crystals come down; the yield of these, however, is very small, if the experiment is carried out as directed. The melting point of these crystals is 172°, which is the same as that of phenylsemicarbazide, a substance originally obtained by Fischer (*Annalen*, **190**, 113) from potassium isocyanate and phenylhydrazine. Its formation is easily explained thus:—

$$CO{<}\begin{matrix}NH_2\\OC_2H_5\end{matrix} + NH_2{\cdot}NH{\cdot}C_6H_5 = CO{<}\begin{matrix}NH_2\\NH{\cdot}NHC_6H_5\end{matrix} + C_2H_5{\cdot}OH.$$

We have also obtained diphenylcarbazide directly from carbamide by the action of an excess of phenylhydrazine.

Pellizzari (*Gazzetta*, **16**, 200), and, more recently, Pinner (*Ber.*, **20**, 2358), have described the action of carbamide in slight excess on phenylhydrazine or its hydrochloride, and have obtained Fischer's phenylsemicarbazide (melting point 172°). From these results, it is evident that both diphenylcarbazide and phenylsemicarbazide may be prepared either from ethylic carbamate or from carbamide. In fact, by heating diphenylcarbazide with carbamide, phenylsemicarbazide results, and conversely, diphenylcarbazide is formed on heating phenylsemicarbazide with phenylhydrazine. It also follows that one amido-group of carbamide is equivalent in its reaction with phenylhydrazine to the ethyl-group of ethylic carbamate.

Diphenylsemicarbazide.

When equivalent quantities of monophenylcarbamide and phenylhydrazine are heated together, ammonia is evolved, and a product is obtained which becomes solid on cooling. This is washed with ether to remove excess of the hydrazine, boiled with water, and the insoluble residue crystallised from alcohol. Rosettes of needles melting at 170—171° separate from the hot alcoholic solution. This substance is diphenylsemicarbazide; it is insoluble in ether and water, but dissolves readily in hot alcohol. The formula $CO<^{NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$ requires:—

	Theory.		Found.	
			I.	II.
C_{13}	156	68·72	68·51	—
H_{13}	13	5·73	6·29	—
N_3	42	18·50	—	18·79
O.....	16	7·04	—	—

The reaction takes place in the following way:—

$$CO<^{NH\cdot C_6H_5}_{NH_2} + NH_2\cdot NH\,C_6H_5 = CO<^{NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5} + NH_3.$$

This substance is a derivative of oxycarbamide, corresponding with the thiocarbamide-derivative, $CS<^{NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$, obtained by Fischer by the action of phenylthiocarbimide on phenylhydrazine. It would doubtless be formed by a similar reaction from phenyl isocyanate and phenylhydrazine.

Phenylsemithiocarbazide.

We expected, by heating a mixture of equivalent quantities of phenylhydrazine and monophenylthiocarbamide, to obtain Fischer's

diphenylsemithiocarbazide, to which we have just referred. On carrying out this experiment, however, ammonia, nitrogen, benzene and aniline were evolved, and a white solid remained; this is phenylsemithiocarbazide. It is insoluble in ether, scarcely soluble in boiling water, but comes down in pinkish crystals from its solution in hot alcohol. These crystals have a melting point of 190°. The formula $CS<^{NH_2}_{NH\cdot NH\cdot C_6H_5}$ requires:—

	Theory.			Found.		
				I.	II.	III.
C_7	84	50·30	p. c.	50·56	—	—
H_9	9	5·39	„	5·86	—	—
S	32	19·16	„	—	19·02	—
N_3	42	25·14	„	—	—	25·57

The reaction by which this substance is produced takes place in two stages. During the first, ammonia is evolved and diphenylsemithiocarbazide is formed thus:—$CS<^{NH_2}_{NH\cdot C_6H_5} + NH_2\cdot NH\cdot C_6H_5 = CS<^{NH\cdot NH\cdot C_6H_5}_{NH\cdot C_6H_5} + NH_3$. The product of this stage, however, cannot be separated, for the second begins before the first is complete, and in it phenylhydrazine converts the diphenylsemithiocarbazide into phenylsemithiocarbazide:—

$$CS<^{NH\cdot NH\cdot C_6H_5}_{NH\cdot C_6H_5} + NH_2\cdot NH\cdot C_6H_5 = CS<^{NH\cdot NH\cdot C_6H_5}_{NH_2} + N_2 + 2C_6H_6.$$

That this reaction actually takes place was shown by a direct experiment on some diphenylsemithiocarbazide.

The formation of aniline probably occurs in the following way, with the direct production of phenylsemithiocarbazide:—

$$CS<^{NH_2}_{NH\cdot C_6H_5} + NH_2\cdot NH\cdot C_6H_5 = CS<^{NH_2}_{NH\cdot NH\cdot C_6H_5} + C_6H_5\cdot NH_2.$$

Pellizzari (*Gazzetta*, **16**, 200) has described a substance which he calls a phenylsemithiocarbazide, formed by the action of phenylhydrazine on thiocarbamide. He states that it melts at 200—201°. If it does, and has the same percentage composition as our substance, it is probably an isomeride in which the phenyl radicle occupies a different position. We hope to settle this point by preparing some of this substance and comparing it with our own.

Colour Reactions.

If a drop of dilute copper sulphate solution is added to a solution of any of these carbazides or semicarbazides, an intense coloration is produced. So intense and distinctive are these colorations that they may be used as qualitative tests. The following colours are very characteristic:—

A few drops of copper sulphate solution produce:—

$CO<^{NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$	Wine-red, destroyed by ammonia and hydrochloric acid.
$CO<^{NH\cdot NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$	Violet colour: ammonia makes it scarlet. Ferric chloride gives a red colour, and an excess destroys it.
$CS<^{NH_2}_{NH\cdot NH\cdot C_6H_5}$	Deep blue, not destroyed by ammonia.
$CS<^{NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$	Green, not destroyed by ammonia.

A solution of copper sulphate added to monophenylcarbamide or monophenylthiocarbamide solution gives no colour reaction. Hence it follows that the production of the colour is characteristic of the substituting hydrazine-group, which is necessary to form the carbazide or semicarbazide. This colour is due to the oxidising action of copper sulphate, for other compounds of similar oxidising action produce colour reactions. Thus, when mercuric chloride is added to diphenylcarbazide, it acquires an intense violet colour very like that produced with copper sulphate.

Phenylurazole.

When a mixture of biuret and phenylhydrazine is heated over a small flame, ammonia is driven off, and, on cooling, the whole mass solidifies. If this is extracted either with alcohol or with water, bundles of crystalline needles separate from the hot solution as it cools. After a second crystallisation from alcohol, these have a melting point of 260°. Their aqueous solution when treated with copper sulphate and potash does not give the "biuret reaction," but on adding potash or ammonia a red coloration is produced.

A determination of the nitrogen in these crystals gave 23·9 per cent. A compound of the formula $C_8H_7N_3O_2$ requires 23·72 per cent. of nitrogen. Such a substance has recently been prepared by Pinner (*Ber.*, **20**, 2358) by heating one part of phenylhydrazine hydrochloride with one and a half parts of carbamide; his product had a melting point of 262°, and it is therefore identical with ours. This

substance, which Pinner has named phenylurazole, is formed in our reaction in the following way:—

$$NH\begin{matrix}CO\cdot NH_2\\CO\cdot NH_2\end{matrix} + \begin{matrix}H\cdot N\cdot H\\|\\H\cdot N\cdot C_6H_5\end{matrix} = NH\begin{matrix}CO\cdot NH\\|\\CO\cdot NC_6H_5\end{matrix} + 2NH_3.$$

Its formation in this way from biuret suggests the idea that in Pinner's reaction biuret is first formed, and it then produces the urazole by reacting with the phenylhydrazine.

Diphenylcarbazide Mercurochloride.

An aqueous solution of mercuric chloride added to an alcoholic solution of the diphenylcarbazide gives at first a deep violet colour, and as the alcohol becomes more dilute, a precipitate is formed. This precipitate is collected and recrystallised from hot alcohol. The crystals are flat plates which do not melt, but decompose suddenly at 135°. A drop of the alcoholic mother-liquor placed on filter-paper produces a deep violet stain.

Analysis showed the crystalline substance to be a double compound of the composition $CO(NH\cdot NH\cdot C_6H_5)_2,HgCl_2$.

	Theory.		Found.		
			I.	II.	III.
C_{13}.....	156	30·40 p. c.	31·04	—	—
H_{14}.....	14	2·73 „	3·00	—	—
N_4.....	56	10·91 „	—	10·99	—
O	16	3·11 „	—	—	—
Hg.....	200	38·99 „	—	—	—
Cl_2	71	13·83 „	—	—	13·87

When this double compound is boiled with water, in which it appears to be insoluble, a liquid tarry substance is formed which floats on the surface, and mercurous chloride falls to the bottom. This viscous tarry substance, on cooling, becomes a brittle, black solid which contains chlorine. It is soluble in alcohol, and on addition of ammonia brings down a violet precipitate of the base which contains no chlorine. An excess of ammonia dissolves the coloured substance, whilst potash makes it red. The dry colour base is soluble in glacial acetic acid with a red coloration. Evidently then the action of mercuric chloride is to oxidise the diphenylcarbazide to the hydrochloride of a colour base which is easily precipitated by ammonia.

Phenylhydrazine Parabanate.

A solution of phenylhydrazine hydrochloride has no action on a

solution of parabanic acid, but on adding sodium acetate to this mixture there is an immediate separation of crystalline leaves, which analysis proves to be phenylhydrazine parabanate. Evidently the reaction takes place quite simply; thus:—

$$C_3O_3N_2H_2,H_2O + 2C_6H_8N_2,HCl + 2NaC_2H_3O_2 = C_3O_3N_2H_2,2(C_6H_8N_2)H_2O + 2NaCl + 2C_2H_4O_2.$$

The same substance may also be prepared by shaking a mixture of the free base with an aqueous solution of the acid. It is quite insoluble in alcohol and ether, and melts at 170° with decomposition. When boiled with a very large quantity of water it dissolves, and at the same time undergoes decomposition with formation of a hydrazide. The substance contains 1 mol. H_2O just in the same way as parabanic acid does. We are inclined to consider this molecule as one of water of crystallisation. The formula $C_3O_3N_2H_2,2(C_6H_8N_2),H_2O$ of the substance dried at 100° requires the following values:—

	Theory.		Found. I.	Found. II.
C_{15}	180	51·73 p. c.	51·23	51·99
H_{20}	20	5·73 „	5·50	5·80
N_6	84	24·13 „	—	—
O_4	64	18·39 „	—	—

Oxalurhydrazide.

When phenylhydrazine parabanate is boiled with a very large excess of water it dissolves slightly, and, on cooling, a yellowish, ramiform, crystalline substance separates. This is oxalurhydrazide. It is very slightly soluble in water, quite insoluble in alcohol and ether, and melts with decomposition at 215°.

The reaction takes place in the following manner:—

$$CO\begin{cases}NH(C_6H_8N_2)\cdot CO \\ | \\ NH(C_6H_8N_2)\cdot CO\end{cases},H_2O = CO<\begin{matrix}NH\cdot CO\cdot CO\cdot NH\cdot NH\cdot C_6H_5 \\ NH_2\end{matrix} + H_2O + C_6H_8N_2.$$

The substance reduces a copper sulphate solution with a green coloration. Our analysis gave the following numbers:—

	Theory.		Found. I.	Found. II.
C_9	108	48·64 p. c.	48·24	—
H_{10}	10	4·50 „	4·91	—
N_4	56	25·22 „	—	25·11
O_3	48	2164 „	—	—

An attempt was made to obtain this same substance from oxaluric acid. The latter was prepared from parabanic acid, according to Liebig's directions; it was then dissolved in water, and treated with sodium acetate and phenylhydrazine hydrochloride solutions. The crystalline silvery plates which immediately separated were collected and well washed with water. The analysis and comparison of this substance with phenylhydrazine oxalate showed that they were identical, so that the following reaction takes place between oxaluric acid and phenylhydrazine hydrochloride:—

$$CO<^{NH\cdot CO\cdot COOH}_{NH_2} + 2C_6H_8N_2,HCl + 2NaC_2H_3O_2 + H_2O =$$
$$2NaCl + CO<^{NH_2}_{NH_2} + \begin{matrix} CO\cdot OH\cdot C_6H_8N_2 \\ | \\ CO\cdot OH\cdot C_6H_8N_2 \end{matrix}.$$

Aniline hydrochloride in presence of sodium acetate gives with parabanic acid a reaction similar to that with phenylhydrazine hydrochloride, and produces aniline parabanate as a precipitate of slender needles; these melt about 250° with decomposition. It may also be directly prepared by shaking aniline with an aqueous solution of parabanic acid.

Phenylhydrazine-alloxan.

The reaction between alloxan in aqueous solution and phenylhydrazine hydrochloride in presence of sodium acetate has lately been described by Pellizzari (*Gazzetta*, **17**, 254). He has stated that the reaction takes place in the following way:—

$$2C_4O_4N_2H_2 + C_6H_5\cdot NH\cdot NH_2 = C_8N_4H_4O_7 + C_6H_6 + N_2 + H_2O.$$

That is to say, that the hydrazine reduces the alloxan to alloxantin, and this he explains by the supposition of the formation of an intermediate substance consisting of 2 mols. of alloxan and 1 mol. of phenylhydrazine, but he has not isolated this substance. We found some time ago that this substance might be easily prepared by mixing cold alcoholic solutions of alloxan and the free base; in a short time a reaction begins, and a substance is precipitated which is extremely unstable, for if the vessel be slightly warmed, an evolution of nitrogen begins. To pour the liquid on a filter-paper is sufficient to start its decomposition. The determination of the composition of this substance by combustion appeared hopeless, and so the following method was adopted. Experiments were made to find the quantity of free nitrogen which a definite weight of alloxan would give, and they proved to our satisfaction that 1 mol. of alloxan yields 1 mol. of

nitrogen; it is probable, therefore, that the intermediate substance has the composition

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)\cdot NH\cdot NH\cdot C_6H_5.$$

The alloxantin is formed by the reaction of this substance with the excess of alloxan, thus:—

Note on a Phenyl-piperyl-thiocarbamide.

This is a crystalline substance prepared by adding phenyl isothiocyanate to piperidine. It is easily recrystallised from alcohol, and melts at 103—104°.

The formula $CS<\begin{matrix}NH\cdot C_6H_5\\NC_5H_{10}\end{matrix}$ requires the following numbers:—

	Theory.			Found. I.	Found. II.
C_{12}	144	65·45	per cent.	65·42	—
H_{16}	16	7·27	,,	7·83	—
N_2	28	12·72	,,	—	13·05
S.....	32	14·54	,,	—	—

University Laboratory, Cambridge,
March, 1888.

XLII.—*Some Derivatives of Phenylmethacrylic Acid.*

By L. Edeleanu, Ph.D.

In the *Berichte* for 1887 (p. 616) I described some derivatives of phenylmethacrylic acid and phenylisobutyric acid, and I have since obtained some further derivatives.

Paranitrophenylisobutyric Acid, $C_6H_4(NO_2)\cdot CH_2\cdot CH(CH_3)\cdot COOH$.

Phenylisobutyric acid, obtained by Conrad and Bischoff's method, is gradually added in small portions to six times its weight of nitric acid, sp. gr. 1·52. On pouring the mixture into cold water, the nitro-

acid is precipitated, and after several crystallisations from alcohol forms small prisms melting at 121°. It is readily soluble in alcohol and acetic acid, but only very slightly in benzene and light petroleum.

Analysis gave—

	$C_{10}H_{11}NO_4$.	I.	II.
C.....	57·42	57·45	—
H.....	5·26	5·43	—
N.....	6·70	—	6·88
O.....	30·62	—	—

The acid forms salts with the alkalis and with barium and strontium, all of which dissolve readily in water. The silver salt is very insoluble. Its analysis gave, dried at 100°, 34·28 per cent. Ag. $C_{10}H_{10}NO_4$ requires 34·21 per cent. Ag.

Oxidation with permanganate yielded an acid which was identified as paranitrobenzoic acid.

Along with the paranitrophenylisobutyric acid of melting point 121° is an acid which remains liquid at the ordinary temperature, and could not be crystallised even on cooling to a low temperature. It forms salts which resemble those of paranitrophenylisobutyric acid, but they are less stable. The silver salt contains 1 mol. H_2O, and is decomposed at 100°; dried over sulphuric acid, it gave 32·49 per cent. Ag; the acid $C_{10}H_{10}NO_4 + OH_2$ requires 32·33 per cent. On oxidation, this acid yields orthonitrobenzoic acid. The liquid acid is, therefore, orthonitrophenylmethacrylic acid.

In order, if possible, to obtain this nitro-acid in a crystalline state, I nitrated the methyl salt, $C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOCH_3$; it is a liquid boiling at 232°.

Analysis gave—

	$C_{11}H_{14}O_2$.	
C.....	74·16	74·35
H.....	7·86	7·90

This was dropped slowly into fuming nitric acid, sp. gr. 1·54, precipitated by much water, and crystallised from ether. The product separated in long prisms, melting at 76°, easily soluble in ordinary solvents. The analysis shows that, in this case, it is converted into a dinitro-derivative.

The results were as follows:—

	$C_{11}H_{12}N_2O_6$.	I.	II.
C.....	49·25	49·26	—
H.....	4·48	4·59	—
N.....	10·45	—	10·45
O.....	35·82	—	—

On warming this nitro-derivative with sulphuric acid for a few minutes, and diluting with water, the acid is liberated, and forms colourless six-sided prisms, somewhat flattened. It melts at 89°, and is very soluble in ordinary solvents.

Analysis gave—

	$C_{10}H_{10}N_2O_6$.	I.	II.
C.....	47·24	47·09	—
H.....	3·92	4·11	—
N.....	11·02	—	11·20
O.....	37·80	—	—

Nitroamidophenylisobutyric Acid,
$NO_2 \cdot C_6H_3(NH_2)CH_2 \cdot CH(CH_3)COOH$,

is obtained from the dinitro-acid by reduction with ammonium sulphide. It crystallises from hot water in bright-red plates which melt at 138°.

Analysis gave :—

	$C_{10}H_{12}N_2O_4$.	I.	II.
C.....	53·57	53·40	—
H.....	5·36	5·48	—
N.....	12·50	—	12·68
O.....	28·57	—	—

Amidomethylhydrocarbostyril, $C_{10}H_{12}N_2O$.

On boiling the nitroamidophenylisobutyric acid with ammonium sulphide for two hours, a substance was obtained which no longer dissolved in ammonia.

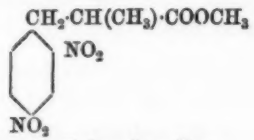
It crystallised from water in slender needles, which melted at 216°, and dissolved with great difficulty in alcohol and light petroleum.

Analysis gave—

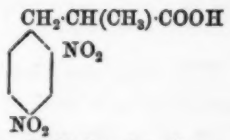
	$C_{10}H_{12}N_2O$.	I.	II.
C.....	68·18	68·30	—
H.....	6·82	7·01	—
N.....	15·91	—	15·95
O.....	9·09	—	—

The formation of this compound leads to the conclusion that one of the nitro-groups in this *dinitrophenylisobutyric acid* is ortho to the fatty part, whilst the second nitro-group is either para or meta. An experiment in which *paranitrophenylisobutyric* was heated with fuming nitric acid produced the same dinitro-acid as above described. The second nitro-group is, therefore, in the para-position to the methane residue.

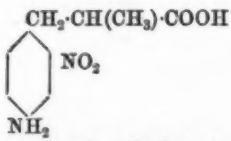
The following formulæ may, therefore, be given as expressing the constitution of these four compounds:—



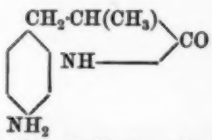
Methyl paraorthodinitrophenylisobutyrate.



Paraorthodinitrophenylisobutyric acid.



Paramido-orthonitrophenylisobutyric acid.



Paramidomethylhydrocarbostyril.

Chemical Laboratory,
Artillery College, Woolwich.

XLIII.—*On the Magnetic Rotatory Power of some of the Saturated and Unsaturated Bibasic Acids and their Derivatives; also of Mesityl Oxide.*

By W. H. Perkin, Ph.D., F.R.S.

Nearly a year since I brought before the Society an account of some experiments upon the magnetic rotatory power of the ethereal salts of maleïc and citraconic acid and their isomers (Proc., 1887–8, p. 98), but owing to a desire to re-examine these substances when prepared by a process different from that previously used, and to extend my experiments on unsaturated compounds, and also to determine the magnetic rotation of some of the saturated bibasic compounds running parallel with them, I delayed sending in any detailed account of my experiments until this additional work was completed. So far as the re-examination of the ethereal salts of the unsaturated acids is concerned, it will be found that the numbers now given do not vary appreciably from those given last year, except in the case of ethylic itaconate, which was a little too high, owing to impurity in the product examined. Before considering, however, the bearing of the results which have been obtained, it will be most convenient first to give the

details of the preparation, properties, and magnetic rotation of the substances examined.

Malonic Acid.

This was examined in aqueous solutions, the proportions corresponding to 1 mol. of acid to 4 mols. of water ($C_3H_4O_4 + 4H_2O$). This is a supersaturated solution at ordinary temperatures. The density determinations gave—

$$d\frac{15°}{15°}\ 1{\cdot}2543, \qquad d\frac{20°}{20°}\ 1{\cdot}2514,$$

$$d\frac{25°}{25°}\ 1{\cdot}2488.$$

The following are the numbers obtained for the magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
23·5°	0·9537	7·460
23·5	0·9543	7·465
23·5	0·9546	7·467
23·5	0·9555	7·474
23·0	0·9605	7·514
23·0	0·9536	7·466
23·0	0·9557	7·477
23·0	0·9545	7·468
Average 23·2	0·9553	7·474
Less mol. rot. of 4 mols. of water		4·000
Malonic acid		3·474

Propyl Succinate.

This ether, which does not appear to have been previously described, was prepared by passing gaseous hydrochloric acid through a hot mixture of succinic acid, and about twice as much propyl alcohol as was necessary for the formation of the ether; when partially saturated with hydrochloric acid, it was gently boiled, so that more succinic acid might go into solution, and again partially saturated with acid, this operation being repeated until all the acid had disappeared; it was then well saturated with hydrochloric acid and allowed to stand about 24 hours. At the end of this time, the product was heated, and the unchanged propyl alcohol distilled off. The crude ether was diluted with ordinary ether, and the solution washed with water and sodium carbonate, after which it was dried over anhydrous potassium

carbonate and distilled. The propyl succinate thus prepared came over within about half a degree, but on taking the densities of different fractions they were not found to agree quite so closely as was desired; the product was therefore carefully fractioned, and was obtained boiling practically constant at 250·8° (corr.), when distilled and collected in two fractions. These gave densities fairly close to each other, viz.:—

Fraction I. $d\frac{15°}{15°}$ 1·0063,

„ II. $d\frac{15°}{15°}$ 1·0061,

The densities found for the other temperatures were—

$d\frac{4°}{4°}$ 1·0157, $d\frac{25°}{25°}$ 0·9986.

Propyl succinate is a colourless oil, boiling without decomposition; when cooled in ice and hydrochloric acid, it solidifies to a crystalline mass which fuses below 0°.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
10·3°	0·9324	10·353
10·3	0·9343	10·373
10·3	0·9345	10·377
13·0	0·9285	10·340
13·0	0·9316	10·374
Average 11·4	0·9323	10·363

Succinyl Chloride.

This was prepared in the ordinary way by means of succinic acid and phosphorus pentachloride. After the oxychloride of phosphorus formed has been mostly distilled off, it is best to fraction the product under reduced pressure, otherwise carbonisation takes place to a considerable extent, especially if a Wurtz flask is used with a neck sufficiently long to contain the thermometer scale in the vapour, and the distillation is conducted slowly. The chloride of succinyl used boiled at 150—152° (corr.) at 214 mm., and was a bright yellow liquid. At 760° it boiled at 190—192° (corr.).

The density determinations gave the following results:—

$d\frac{4^\circ}{4^\circ}$ 1·4252, $d\frac{20^\circ}{20^\circ}$ 1·4073,

$d\frac{10^\circ}{10^\circ}$ 1·4178, $d\frac{25^\circ}{25^\circ}$ 1·4028,

$d\frac{15^\circ}{15^\circ}$ 1·4123, $d\frac{30^\circ}{30^\circ}$ 1·3809.

t.	Sp. rotation.	Mol. rotation.
10·4°	1·1893	7·224
10·0	1·1888	7·219
10·0	1·1870	7·209
10·0	1·1879	7·214
9·0	1·1966	7·261
9·2	1·1996	7·280
9·5	1·1957	7·255
9·7	1·1951	7·256
11·0	1·1901	7·234
12·0	1·1946	7·267
13·0	1·1871	7·227
14·0	1·1916	7·265
Average 10·6	1·1919	7·242

Pyrotartaric Anhydride and Chloride.

The method given for the preparation of pyrotartaric anhydride consists in heating pyrotartaric acid with phosphorus pentasulphide (Böttinger, *Ber.*, **11**, 1352). At first it was intended to prepare it by heating pyrotartaric chloride with the acid, but the yield of chloride obtained was very unsatisfactory, as carbonisation took place to a considerable extent. The chloride boiled at about 210—220° under 760 mm., and at about 158° at 214 mm. If the operation had been conducted from the first under reduced pressure, probably a more satisfactory yield might have been obtained. The process, which was found to work well for the production of the anhydride, consists in digesting the powdered acid with an excess of acetyl chloride until all action is over, and slowly fractioning the product, when the anhydride is eventually obtained as a rather thick colourless oil, boiling constantly at 247·4 (corr.). This boiling point is lower than that of succinic anhydride, which is given as 250°, whilst that of glutaric anhydride is given as 282—287°. Pyrotartaric anhydride has little or no odour; it sinks as an oil in cold water, but when agitated with hot water it soon dissolves, yielding a perfectly clear solution. It remains fluid even if cooled down to near 0°, and has been described as an oil, but if rubbed with a glass rod crystallisation sets

in and it soon becomes a white confused crystallised mass. This fuses at 31·5—32°, but not sharply.

The relative density determinations gave—

$d\frac{6\cdot5^\circ}{6\cdot5^\circ}$ 1·2458, $d\frac{40^\circ}{40^\circ}$ 1·2203,

$d\frac{15^\circ}{15^\circ}$ 1·2378, $d\frac{55\cdot8^\circ}{55\cdot8^\circ}$ 1·2122.

$d\frac{25^\circ}{25^\circ}$ 1·2303,

From these the following true densities were deduced :—

t.	*d.*	Difference.
0°	1·2526	
		0·0104
10	1·2422	
		0·0104
20	1·2318	
		0·0104
30	1·2214	
		0·0104
40	1·2110	
		0·0104
50	1·2006	
		0·0104
60	1·1902	

The determinations of the magnetic rotation gave—

t.	Sp. rotation.	Mol. rotation.
9·4°	0·9323	4·750
9·0	0·9335	4·755
9·0	0·9359	4·767
8·5	0·9383	4·777
17·2	0·9259	4·744
16·3	0·9371	4·789
Average 11·6	0·9338	4·764

The following were made at higher temperatures :—

t.	Sp. rotation.	Mol. rotation.
47·8°	0·9096	4·738
49·4	0·9104	4·743
50·9	0·9075	4·730
52·1	0·9079	4·737
Average 50·0	0·9088	4·737

Glutaric Acid.

This acid was prepared from the cyanide of trimethylene which is obtained on digesting bromide of trimethylene with cyanide of potassium and alcohol. The cyanide was purified by distillation and then saponified with aqueous potash. The reaction takes place easily, ammonia being evolved very freely on heating the mixture. The resulting solution was acidified with hydrochloric acid and the glutaric acid taken up with ether; it is necessary to agitate the solution many times successively with fresh quantities of ether before all the acid is taken up. In one operation the acidified mixture was evaporated to dryness before extraction with ether, but the acid obtained was coloured and difficult to get quite pure.

The acid obtained from the ethereal solution was dried over the water-bath and crystallised from benzene. This was found to be a convenient solvent, glutaric acid being moderately soluble in it when boiling, and but slightly so when cold. After two crystallisations it was obtained in white, non-deliquescent plates melting at 96—97°. Rebout gives 96·5° (*Ann. Chem. Phys.* [5], **14**, 501).

The strongest solution of this acid which could be conveniently used for the examination of its magnetic rotation was in the proportion of 1 mol. of acid to 10 mols. of water ($C_5H_8O_4 + 10OH_2$). Two such solutions were made, for the second the acid was recrystallised from water. They had the following densities:—

Sol. I.	Sol. II.
$d\frac{4^\circ}{4^\circ}$ 1·1224,	
$d\frac{15^\circ}{15^\circ}$ 1·1166,	$d\frac{15^\circ}{15^\circ}$ 1·1162.
$d\frac{25^\circ}{25^\circ}$ 1·1126,	

The following numbers were obtained for the magnetic rotation:—

Solution I.

t.	Sp. rotation.	Mol. rotation.
12·6°	1·0001	15·509
13·0	1·0008	15·521
13·0	1·0005	15·516
13·3	0·9992	15·500
13·6	0·9933	15·410
13·6	0·9992	15·502
14·2	0·9980	15·500
Average 13·3	0·9987	15·494

Solution II.

	t.	Sp. rotation.	Mol. rotation.
	16·4°	0·9911	15·428
	16·4	0·9949	15·488
	16·4	0·9934	15·465
	16·4	0·9946	15·483
	16·4	0·9970	15·492
Average	16·4	0·9942	15·471

These numbers are as close as could be expected; the average of the molecular rotation, less the molecular rotation of 10 mols. of water, should give that of glutaric acid, thus:—

Average mol. rot. of $C_5H_8O_4 + 10OH_2 = 15{\cdot}482$
Less molecular rotation of $10OH_2 \ldots . = 10{\cdot}000$

Molecular rotation of glutaric acid ... = 5·482

Ethyl Glutarate.

The ethyl compound of glutaric acid was prepared by saturating its alcoholic solution with hydrochloric acid. The ether, after being separated by means of water, was washed with sodium carbonate, dried with potassium carbonate, and distilled. It nearly all came over at 236° (corr.), a little of the first and last being rejected. Rebout gives 236·5—237° (corr.) as the boiling point he observed. The density determinations gave:—

$d\frac{4^\circ}{4^\circ}$ 1·0382, $d\frac{20^\circ}{20^\circ}$ 1·0243,

$d\frac{10^\circ}{10^\circ}$ 1·0327, $d\frac{25^\circ}{25^\circ}$ 1·0204,

$d\frac{15^\circ}{15^\circ}$ 1·0284, $d\frac{30^\circ}{30^\circ}$ 1·0167.

The following are the numbers obtained for the magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
12·6°	0·9219	9·345
12·6	0·9232	9·357
12·6	0·9235	9·361
12·9	0·9250	9·379
12·9	0·9259	9·388
12·9	0·9251	9·380
11·3	0·9206	9·322
11·3	0·9221	9·337
11·3	0·9243	9·359
11·3	0·9243	9·359
12·0	0·9221	9·342
13·3	0·9240	9·372
13·6	0·9195	9·329
13·9	0·9214	9·350
Average 12·5	0·9231	9·356

Ethyl Sebate.

The specimen examined was the same as that described in my previous paper (Trans., 1884, 518). The following fresh measurements were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
11·2°	0·9773	14·423
11·2	0·9782	14·436
11·3	0·9802	14·467
11·5	0·9829	14·508
12·0	0·9791	14·459
Average 11·4	0·9795	14·459

Maleic Anhydride.

This was prepared by the process described by me in a paper brought before the Society some years since (Trans., 1881, 561), and consists in digesting maleic acid with acetyl chloride, and decomposing the resulting aceto-maleic anhydride by distillation. Considerable quantities were made and the process was found to work very satisfactorily. It was found safest to use a good excess of acetyl chloride, otherwise, if too little be used, fumaric acid will be formed and come over with the last portion of maleic anhydride. The latter should be distilled three or four times to ensure the complete decomposition of the aceto-maleic anhydride, and fraction off the acetic acid formed.

The boiling points of these preparations were taken with different thermometers, and gave :—I, 199·5° corr.; II, 200° corr.; III, 200° corr.; so that practically the boiling point of maleic anhydride may be taken as 200°.

Maleic anhydride may be crystallised from absolute alcohol if the operation be conducted quickly, but if left to stand afterwards the crystals gradually disappear.

This substance being solid its magnetic rotation was determined from its solutions in acetic acid, acetic anhydride, and citraconic anhydride.

Solution of Maleic Anhydride in Acetic Acid.

The acetic acid solution was made in the proportion of 2 mols. of acetic acid to 1 mol. of maleic anhydride, $2C_2H_4O_2 + C_4H_2O_3$. This solution was a supersaturated one and the anhydride crystallised out on standing, but, after warming, the solution remained free from crystals sufficiently long for the required determination. The acetic acid used was perfectly free from water. The density determinations gave the following numbers :—

$$d\frac{10°}{10°}\ 1{\cdot}1880, \qquad d\frac{17°}{17°}\ 1{\cdot}1804,$$

$$d\frac{25°}{25°}\ 1{\cdot}1733.$$

The magnetic rotation found was as follows :—

t.	Sp. rotation.	Mol. rotation.
23·0°	0·9219	9·502
24·0	0·9204	9·494
24·5	0·9204	9·498
25·0	0·9201	9·498
Average 24·1	0·9207	9·498
Less mol. rot. of 2 mols. $C_2H_4O_2$		5·050
Mol. rot. of 1 mol. $C_4H_2O_3$		4·448

Solution of Maleic Anhydride in Acetic Anhydride.

The solution of maleic anhydride in acetic anhydride was in the proportion of 5 mols. of maleic anhydride to 2 mols. of acetic anhydride, $5C_4H_2O_3 + 2C_4H_6O_3$. This forms a supersaturated solution which sometimes will remain liquid for a long time, but is very

uncertain in this particular. Its relative density determinations gave the following numbers:—

$d\frac{6{\cdot}6^\circ}{6{\cdot}6^\circ}$ 1·2781, $d\frac{60^\circ}{60^\circ}$ 1·2345,

$d\frac{25^\circ}{25^\circ}$ 1·2595, $d\frac{98^\circ}{98^\circ}$ 1·2158.

$d\frac{39{\cdot}9^\circ}{39{\cdot}9^\circ}$ 1·2480,

From these the following true densities were deduced:—

t.	*d.*	Difference.	*t.*	*d.*	Difference.
10°	1·2740	0·0118	60°	1·2142	0·0121
20	1·2622	0·0119	70	1·2019	0·0123
30	1·2503	0·0120	80	1·1896	0·0123
40	1·2383	0·0120	90	1·1772	0·0124
50	1·2263		100	1·1648	0·0124

The magnetic rotation gave the following numbers. Owing to the tendency of the solution to crystallise, the determinations had to be made at a rather high temperature. This will make the results probably a little low:—

t.	Sp. rotation.	Mol. rotation.
32°	0·9972	30·661
31	0·9999	30·733
30	0·9973	30·645
29·2	0·9958	30·564
Average 30·7	0·9975	30·651
Less mol. rot. of 2 mols. $C_4H_6O_3$		8·564
Mol. rot. of 5 mols. $C_4H_2O_3$ ..		22·087
„ 1 mol. „ ..		4·417

Solution of Maleic Anhydride in Citraconic Anhydride.

Maleic anhydride dissolves easily in citraconic anhydride; the proportions used were equimolecular, $C_4H_2O_3 + C_5H_4O_3$. This solution deposits maleic anhydride in cold weather. The density determinations of this solution gave—

$d\frac{15°}{15°}$ 1·2983, $d\frac{20°}{20°}$ 1·2938,

$d\frac{25°}{25°}$ 1·2896.

The magnetic rotations gave the following numbers :—

t.	Sp. rotation.	Mol. rotation.
19·5°	1·1206	10·101
19·0	1·1198	10·091
18·5	1·1216	10·103
18·0	1·1193	10·080
Average 18·8	1·1203	10·069
Less mol. rot. of specimen of $C_5H_4O_3$ used		5·527
Mol. rot. $C_4H_2O_3$.		4·542

A second solution of maleic anhydride in citraconic anhydride was also examined, the citraconic anhydride used as the solvent being that purified with phosphoric anhydride, and described further on in this paper; the proportions used were equimolecular. The density determinations of this product gave—

$d\frac{10°}{10°}$ 1·3039, $d\frac{15°}{15°}$ 1·2992,

$d\frac{25°}{25°}$ 1·2946.

These numbers are slightly higher than those obtained with the previous preparations, owing to the density of the citraconic anhydride used being higher. The magnetic rotation gave the following numbers :—

t.	Sp. rotation.	Mol. rotation.
12·1°	1·1250	10·075
10·6	1·1262	10·090
9·75	1·1296	10·105
9·40	1·1296	10·103
9·0	1·1275	10·081
9·0	1·1269	10·076
Average 9·94	1·1275	10·088
Less mol. rot. of specimen of $C_5H_4O_3$ used		5·540
Mol rot. $C_4H_2O_3$.....		4·548

Maleic Acid.

The acid being solid and not easily fusible had to be examined in solution. The strongest solution it was found practical to use was in the proportion of 1 mol. of maleic acid to 8 mols. of water ($C_4H_4O_4 + 8OH_2$). This was a supersaturated solution, and the acid was deposited to some extent on standing. Its density determinations gave—

$$d\frac{15°}{15°}\ 1{\cdot}1694, \qquad d\frac{20°}{20°}\ 1{\cdot}1676,$$

$$d\frac{25°}{25°}\ 1{\cdot}1656.$$

The magnetic rotation found was as follows:—

t.	Sp. rotation.	Mol. rotation.
26·0°	1·0972	13·609
26·0	1·1002	13·646
26·0	1·0981	13·621
26·0	1·0975	13·644
24·0	1·0994	13·628
24·0	1·1028	13·670
23·0	1·1002	13·627
23·0	1·0999	13·624
Average 24·8	1·0994	13·633
Less mol. rot. of 8 mols. OH_2 ..		8·000
Maleic acid		5·633

Ethyl Maleate.

Several experiments were made on the preparation of this compound which it may be useful to describe. Attempts were first made to produce it directly from alcohol and maleic anhydride, but to get a neutral ether it is necessary to employ a high temperature; the mixture was therefore heated in sealed tubes at 180—190° for four or five hours, but in this way the product obtained consisted chiefly of ethyl fumarate. Maleic anhydride was then digested with alcohol, the mixture cooled in ice and salt, and saturated with hydrochloric acid gas previously cooled by passing through a worm placed in a freezing mixture; at this low temperature the action did not take place, and it was necessary to allow the product to attain a temperature of 18° or 19° to induce etherification. The product obtained consisted chiefly of ethyl maleate, but it contained a little ethyl

fumarate and a small quantity of some chlorine addition product. As these methods did not yield satisfactory products, recourse was had to the process of preparing this ether from silver maleate by acting on it with ethyl iodide. In carrying this out, the silver salt was added to an excess of ethyl iodide little by little, the heat of a water-bath being applied to set up the reaction after each addition; the product was then digested on the water-bath for a short time. The ethyl maleate was then extracted from the silver iodide by means of dry ether, and the ethereal solution distilled until the residual liquid had attained a temperature of about 160°, this was then fractioned under reduced pressure. The ethyl maleate thus prepared came over at 180·5 (corr.) at 212 mm.; it also boiled at 223·5° at 760 mm. (Anschutz found 225°). It was found to be free from ethyl fumarate.

The following has been found the most satisfactory method of testing ethyl maleate for small quantities of ethyl fumarate. About 2 or 3 c.c. of the ether are saponified with alcoholic potash to which some *water* has been added, the mixture is then diluted with water and the alcohol boiled off. After cooling, dilute hydrochloric acid is added in excess, and if no fumaric acid crystallises out, the solution is treated with ether, which will remove every trace of fumaric acid, but scarcely any maleic acid, so that on evaporation the former, if present, will be found to constitute most of the residue.

Neutral salts of maleic acid give with ferric salts a red solution similar to that formed by an acetate, but fumarates give a bulky, pale-brown precipitate; probably these reactions might be used for testing the purity of ethyl maleate, but in this case it is especially necessary to saponify the ether with alcoholic potash diluted with water, otherwise, apparently an addition product is formed with the ethyl maleate which yields a potash salt, precipitating ferric salts in a similar way to fumarates.

The relative density determinations of ethyl maleate gave—

$$d\frac{10^\circ}{10^\circ}\ 1{\cdot}0780, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}0695,$$

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}0735, \qquad d\frac{25^\circ}{25^\circ}\ 1{\cdot}0658.$$

The following numbers were obtained for the magnetic rotation of this compound :—

	t.	Sp. rotation.	Mol. rotation.
	12·0°	1·0871	9·649
	11·6	1·0861	9·637
	11·6	1·0856	9·632
	11·6	1·0842	9·620
	12·5	1·0857	9·640
	12·5	1·0857	9·640
	12·5	1·0879	9·660
	11·0	1·0877	9·646
	10·5	1·0878	9·643
	23·0	1·0730	9·608
	23·0	1·0702	9·582
	22·0	1·0702	9·576
	22·0	1·0725	9·596
Average	15·1	1·0818	9·625

Ethyl Fumarate.

The first specimen examined was prepared by saturating a mixture of alcohol and fumaric acid with gaseous hydrochloric acid, the mixture being heated now and then until the acid disappeared. The ether was washed first with water, and then with sodium carbonate, dried and fractioned. It boiled at 219—220° (corr.), but contained a small quantity of chlorine from the formation of ethyl chlorosuccinate. Dr. Purdie also observed the formation of ethyl chlorosuccinate when preparing ethyl fumarate by this method, though he evidently obtained more of it than I did, probably on account of continuing the application of heat to the mixture whilst passing the hydrochloric acid (Trans., 1881, **39**, 346).

The density determination gave—

$$d\frac{15°}{15°}\ 1{\cdot}0623, \qquad d\frac{25°}{25°}\ 1{\cdot}0539.$$

The magnetic rotation determinations gave—

	t.	Sp. rotation.	Mol. rotation.
	9·5°	1·1247	10·073
	9·5	1·1231	10·064
	12·8	1·1273	10·165
	12·8	1·1251	10·145
Average	11·1	1·1250	10·112

As this ether was not quite pure, other experiments were made on its preparation, and it was found that etherification might be

effected by heating the acid and alcohol in a sealed tube to a high temperature. The proportions used were one of fumaric acid to three of absolute alcohol, the mixture being heated at 180—190° for seven or eight hours. The excess of alcohol was then distilled off, and the ethyl fumarate washed with water and sodium carbonate, dried, and distilled; it boiled at 219·3° (corr.). Its density determinations gave—

$d\frac{10°}{10°}$ 1·0626, $d\frac{20°}{20°}$ 1·0535,

$d\frac{15°}{15°}$ 1·0578, $d\frac{25°}{25°}$ 1·0496.

As might be expected these densities are somewhat lower than those of the ether containing chlorine.

The magnetic rotations found were as follows:—

	t.	Sp. rotation.	Mol. rotation.
	10·0°	1·1256	10·119
	10·0	1·1280	10·150
	10·5	1·1253	10·130
	10·5	1·1232	10·111
	22·5	1·1135	10·119
	21·7	1·1133	10·111
	21·5	1·1126	10·103
Average	15·2	1·1202	10·120

The numbers are therefore almost identical with those obtained with the previous less pure specimen of ethyl fumarate; the influence of a small quantity of ethyl chlorosuccinate would only very slightly reduce the rotation. The rotation of ethyl chlorosuccinate deduced from other compounds which have lately been examined, is 9·72, or very close to that number.

Fumaryl Chloride.

This was prepared from fumaric acid by means of phosphorus pentachloride. It was obtained as a pale-yellow fuming liquid boiling at 161—164°. Its density determinations gave—

$d\frac{15°}{15°}$ 1·4202, $d\frac{20°}{20°}$ 1·4149,

$d\frac{25°}{25°}$ 1·4095.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·0°	1·4579	8·739
17·0	1·4567	8·732
16·8	1·4564	8·729
16·8	1·4579	8·738
14·3	1·4641	8·758
13·9	1·4652	8·763
13·2	1·4637	8·769
Average 15·6	1·4607	8·747

Citraconic Anhydride.

This was prepared in the ordinary way by the distillation of citric acid. It was fractioned many times. The product selected for examination boiled at 213·5—214° (corr.). Its density determinations gave—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}2605, \qquad d\frac{15^\circ}{15^\circ}\ 1{\cdot}2493,$$

$$d\frac{10^\circ}{10^\circ}\ 1{\cdot}2540, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}2450,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}2409.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
15·5°	1·1014	5·488
17·0	1·1125	5·547
18·5	1·1113	5·548
14·0	1·1113	5·530
13·5	1·1141	5·544
14·0	1·1100	5·525
22·0	1·1014	5·512
21·5	1·1011	5·509
21·0	1·1011	5·494
20·5	1·1039	5·519
Average 17·7	1·1068	5·522

As these numbers were not so high as was expected, it was thought that the citraconic anhydride might contain some citraconic acid; it was, therefore, heated with phosphoric anhydride up to its boiling point. As the latter was apparently a good deal hydrated, and also blackened, the citraconic anhydride was decanted, and heated with fresh phosphoric anhydride, this operation being repeated a third

time; altogether a considerable quantity of phosphoric anhydride was used. The citraconic anhydride was then decanted from the phosphoric anhydride and fractioned; it commenced to distil at 213·5° (corr.), and about nine-tenths came over within a degree of this. This distillate was again treated with phosphoric anhydride, and heated up to its boiling point for a short time with it, when the phosphoric anhydride was now only a little discoloured; after decanting off the citraconic anhydride it was again distilled, when it came over nearly constantly at 213·5°, a few drops at the last which were rejected coming over at 215°.

Citraconic anhydride thus purified was perfectly colourless, and a more mobile fluid than the ordinary product. Its relative density determinations gave—

$d\frac{4^\circ}{4^\circ}$ 1·2617,	$d\frac{51\cdot45^\circ}{51\cdot45^\circ}$ 1·2246,
$d\frac{15^\circ}{15^\circ}$ 1·2504,	$d\frac{59\cdot75^\circ}{59\cdot75^\circ}$ 1·2205,
$d\frac{20^\circ}{20^\circ}$ 1·2461,	$d\frac{65^\circ}{65^\circ}$ 1·2178,
$d\frac{25^\circ}{25^\circ}$ 1·2420,	$d\frac{77\cdot5^\circ}{77\cdot5^\circ}$ 1·2119,
$d\frac{25\cdot92^\circ}{25\cdot92^\circ}$ 1·2418,	$d\frac{87\cdot75^\circ}{87\cdot75^\circ}$ 1·2081,
$d\frac{37\cdot4^\circ}{37\cdot4^\circ}$ 1·2335,	$d\frac{98\cdot6^\circ}{98\cdot6^\circ}$ 1·2055.

These numbers are averages of two and in some cases of three determinations. The following true densities were deduced from them:—

t.	*d.*	Diff.
0°	1·2659	
		0·0110
10	1·2549	
		0·0110
20	1·2439	
		0·0111
30	1·2328	
		0·0110
40	1·2218	
		0·0111
50	1·2107	
		0·0110
60	1·1997	
		0·0111
70	1·1886	
		0·0111
80	1·1775	
		0·0111
90	1·1664	
		0·0111
100	1·1553	

The following numbers were obtained for its magnetic rotation.

Two series of determinations were made—one at the ordinary temperature, and one at a high temperature for reasons explained further on.

Series I. Ordinary Temperature.

t.	Sp. rotation.	Mol. rotation.
17·8°	1·1101	5·535
17·8	1·1131	5·550
17·8	1·1098	5·533
17·8	1·1137	5·553
16·5	1·1131	5·544
17·0	1·1107	5·534
17·5	1·1101	5·534
Average 17·4	1·1115	5·540

It will be observed that the specific rotation of this purified citraconic anhydride is higher than that of the ordinary product, but that the molecular rotation is practically the same. This is accounted for by the increase of the density resulting from the purification.

Series II. High Temperatures.

t.	Sp. rotation.	Mol. rotation.
60·5°	1·0693	5·451
64·7	1·0790	5·511
66·2	1·0687	5·461
67·1	1·0708	5·461
67·4	1·0708	5·475
67·7	1·0714	5·477
Average 65·7	1·0717	5·473

Citraconic Anhydride and Acetic Acid.

This mixture was made to correspond to the analogous one containing maleic anhydride, being in the proportions of 1 mol. of anhydride to 2 mols. of acetic acid. The density determinations gave—

$d\frac{10°}{10°}$ 1·1508, $d\frac{20°}{20°}$ 1·1413,

$d\frac{15°}{15°}$ 1·1459, $d\frac{25°}{25°}$ 1·1371.

The numbers obtained for the magnetic rotation were as follows:—

t.	Sp. rotation.	Mol. rotation.
23·2°	0·9294	10·519
23·2	0·9261	10·483
23·2	0·9281	10·506
23·2	0·9261	10·482
Average 23·2	0·9274	10·498
Less 2 mols. acetic acid		5·050
Citraconic anhydride		5·448

Citraconic Anhydride and Acetic Anhydride.

This mixture was also examined so as to compare the results with those obtained with maleic anhydride and acetic anhydride. The quantities used were in the proportion of 5 mols. of citraconic anhydride to 2 mols. of acetic anhydride.

The relative density determinations gave the following results:—

$d\frac{6{\cdot}7°}{6{\cdot}7°}$ 1·2116, $d\frac{59{\cdot}8°}{59{\cdot}8°}$ 1·1704,

$d\frac{15°}{15°}$ 1·2028; $d\frac{64{\cdot}75°}{64{\cdot}75°}$ 1·1676;

$d\frac{25°}{25°}$ 1·1941, $d\frac{98{\cdot}05°}{98{\cdot}05°}$ 1·1544.

The true densities deduced from these are as follows:—

t.		Difference.
10°	1·2078	
		0·0118
20	1·1960	
		0·0116
30	1·1844	
		0·0114
40	1·1730	
		0·0112
50	1·1618	
		0·0112
60	1·1506	
		0·0112
70	1·1394	
		0·0111
80	1·1283	
		0·0111
90	1·1172	
		0·0111
100	1·1061	

The following results were obtained for the magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·0	1·0192	35·982
15·5	1·0198	36·003
15·5	1·0198	36·005
15·5	1·0186	35·961
Average 15·6	1·0193	35·988
Less 2 mols. acetic anhydride ..		8·564
		5) 27·485
Citraconic anhydride		5·497

Citraconic Acid.

As this acid is solid, it was found necessary to examine its solutions. The solution employed was made in the proportions of 1 mol. of citraconic acid to 2 mols. of water ($C_5H_6O_4 + 2OH_2$), and was prepared by mixing citraconic anhydride with water in the proportion of 1 mol. of anhydride to 3 mols. of water. The resulting product was a supersaturated solution, depositing part of the acid on standing. A solution of citraconic acid when evaporated on the water-bath decomposes, and on adding water to it citraconic anhydride separates as an oil. Crystallised citraconic acid kept over sulphuric acid under a bell-jar smells strongly of the anhydride.

The density determinations of the above aqueous solution of citraconic acid gave the following results:—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}2410, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}2392.$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}2366,$$

The numbers obtained for the magnetic rotation were as follows:—

t.	Sp. rotation.	Mol. rotation.
25·0°	1·1469	8·553
25·0	1·1471	8·555
25·0	1·1480	8·562
25·0	1·1496	8·573
23·0	1·1504	8·572
23·0	1·1525	8·689
23·0	1·1492	8·564
Average 24·1	1·1491	8·567
Less 2 mols. water.....		2·000
Citraconic acid		6·567

Ethyl Citraconate.

This was in the first instance prepared by saturating an alcoholic solution of citraconic anhydride with hydrochloric acid gas, keeping the mixture cool. After standing a few hours, the ether was separated by the addition of water, washed with dilute sodium carbonate, dried over potassium carbonate, and distilled. Thus obtained it boiled at 230·5 (corr.). The density determinations gave—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}0486, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}0445,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}0414.$$

The magnetic rotation determinations gave—

t.	Sp. rotation.	Mol. rotation.
19·0°	1·0650	10·524
16·0	1·0705	10·557
17·5	1·0651	10·514
18·8	1·0638	10·510
21·5	1·0573	10·490
20·0	1·0598	10·481
Average 18·4	1·0636	10·513

On treating this ether with alcoholic soda, and testing the resulting product, it was found to contain a little chlorine, showing the presence of some chlorine addition product resulting from the union of the ethyl citraconate with the hydrochloric acid used in its preparation.

Experiments were therefore made to obtain this ether in a purer condition by heating citraconic anhydride with absolute alcohol in sealed tubes. By employing a temperature of 120—130° for a day, a considerable quantity of an oily product was obtained, but as it mostly dissolved in a solution of sodium carbonate, it was evidently the acid ether; a temperature of about 180—200° was therefore used and maintained for six or seven hours; after distilling off the alcohol, the product was washed with sodium carbonate solution, dried over potassium carbonate and distilled, it boiled almost constantly at 230·3°. The density determinations gave—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}0485, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}0446,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}0409.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	10·0°	1·0707	10·515
	10·4	1·0673	10·484
	10·8	1·0689	10·503
	11 2	1·0666	10·483
	11·5	1·0695	10·514
	13·5	1·0497	10·484
	13·5	1·0526	10·513
Average	11·6	1·0636	10·499

Some time after these experiments were made, a quantity of the ethyl citraconate used for them was saponified, the solution acidified, and the liberated acid taken up with ether. On gently evaporating this, citraconic acid was left as a syrupy liquid owing to the presence of a little water; but after standing for several days it deposited small crystals of a less soluble acid, evidently either itaconic or citraconic acid, which had been formed by the high temperature used when preparing the ether, it was therefore finally resolved to prepare some pure ethyl citraconate from silver citraconate and ethyl iodide.

Silver citraconate comes down as a very bulky precipitate, quite different in character from silver itaconate, and does not become dense when heated to 100°. It is difficult to wash, unless a vacuum pump is used with a considerable reduction of pressure. It was dried at 100°, and gradually added to a large excess of colourless ethyl iodide. The action did not set in quickly in the cold, but when gently heated, local boiling took place on each addition of the salt. After all the silver salt had been added, the mixture was heated on the water-bath for a short time, and the silver iodide collected on a filter and washed with ethyl iodide. The filtrate was then freed from ethyl iodide by distillation, and the ethyl citraconate washed with sodium carbonate solution, dried by means of potassium carbonate, and distilled. The ethyl citraconate thus obtained boiled constantly at 230·3°, and was perfectly colourless. Its density determinations gave—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}0567, \qquad d\frac{15^\circ}{15^\circ}\ 1{\cdot}0468,$$

$$d\frac{10^\circ}{10^\circ}\ 1{\cdot}0514, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}0429,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}0395.$$

It will be observed that the density of the ethyl citraconate

prepared in this manner is slightly lower than that of the products previously described.

The numbers obtained for its magnetic rotation are as follows :—

	t.	Sp. rotation.	Mol. rotation.
	18·3°	1·0651	10·540
	18·4	1·0655	10·543
	18·3	1·0643	10·532
	18·4	1·0604	10·494
	17·0	1·0613	10·492
	17 0	1·0632	10·514
	17·0	1·0627	10·507
Average	17·8	1·0632	10·517

The three specimens have therefore given numbers very close to each other, the influence of the small amount of impurities in the two first being compensated to a great extent by the variation in density, &c. The average of all the numbers gives 10·500 practically.

Methyl Citraconate.

This was prepared from silver citraconate and methyl iodide in the same way as the ethylic salt just described; it boiled very nearly constantly at 210·5° (corr.), and was perfectly colourless. The density determinations gave—

$d\frac{4°}{4°}$ 1·1312, $d\frac{20°}{20°}$ 1·1168,

$d\frac{10°}{10°}$ 1·1251, $d\frac{25°}{25°}$ 1·1131,

$d\frac{15°}{15°}$ 1·1208, $d\frac{30°}{30°}$ 1·1098.

The following are the numbers obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	13·3°	1·0675	8·349
	13·0	1·0689	8·359
	13·0	1·0703	8·370
	12·6	1·0634	8·371
	12·6	1·0709	8·372
Average	12·9	1·0682	8·364

Ethyl Itaconate.

The acid used in the following experiment was obtained from Kahlbaum. An attempt was made to etherify the acid by means of alcohol and hydrochloric acid, but as it seemed to rapidly form an additive product with the hydrochloric acid it was abandoned. The method employed for the preparation of ethyl fumarate already described was then adopted, the mixture of itaconic acid and absolute alcohol being heated for seven or eight hours at 180—190°. The ether thus prepared boiled at 227·5—228°, and its density determinations gave—

$$d\frac{7°}{7°}\ 1{\cdot}0563, \qquad d\frac{15°}{15°}\ 1{\cdot}0490,$$

$$d\frac{25°}{25°}\ 1{\cdot}0412.$$

The magnetic rotation determined from 15 series of observations gave a *molecular rotation* of 10·630, the details of which it is useless to give, as the ether made by the above process is evidently not pure. Suspicion was aroused on account of the rotation of the compound being higher than it was expected to be; the impurity is probably due to ethyl mesaconate formed by the high temperature employed. This ether was prepared more than 12 months since and kept in the dark, but on redetermining its density it was found that a certain amount of change, probably polymerisation, had taken place. The density at $d\frac{15°}{15°}$ had increased to 1·0537 or 0·0047, and, on distilling, about four-fifths came over at 227·7—228°, some higher boiling product being left behind.

To obtain the ether pure, the method of treating the silver salt with ethyl iodide was again resorted to. Silver itaconate is apparently crystalline, and much more dense than silver citraconate, moreover, it is not so easily acted on by ethyl iodide as that salt, and requires digesting with it for some time on the water-bath to complete the reaction. On distilling the ethyl itaconate prepared by this method, about five-sixths came over below 230°, leaving a residue which partly came over only after being strongly heated, in fact, the residue appears to consist of ethyl itaconate more or less polymerised.

The first portion of the distillate on being fractioned gave ethyl itaconate with a boiling point of 227 7—227·9°. The density determinations gave—

$$d\frac{4°}{4°}\ 1{\cdot}0607, \qquad d\frac{10°}{10°}\ 1{\cdot}0546,$$

$d\frac{15^\circ}{15^\circ}$ 1·0504, $d\frac{20^\circ}{20^\circ}$ 1·0464,

$d\frac{25^\circ}{25^\circ}$ 1·0427.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
18·0°	1·0598	10·449
18·0	1·0601	10·453
18·0	1·0601	10·453
18·0	1·0607	10·457
17·0	1·0647	10·491
17·0	1·0640	10·484
17·0	1·0647	10·484
Average 17·6	1·0620	10·467

It will be seen that this ether prepared from the silver salt does not differ in boiling point from that obtained by heating itaconic acid with alcohol; its density, however, is slightly higher, whilst the specific and molecular rotations are appreciably lower.

Ethyl Mesaconate.

This ether was prepared by saturating a mixture of alcohol and mesaconic acid with gaseous hydrochloric acid. The ether was washed with dilute sodium carbonate, dried, and distilled. It was free from chlorine. The boiling point was 228° (corr.).

The density determinations gave the following numbers :—

$d\frac{4^\circ}{4^\circ}$ 1·0598, $d\frac{15^\circ}{15^\circ}$ 1·0492,

$d\frac{10^\circ}{10^\circ}$ 1·0539, $d\frac{20^\circ}{20^\circ}$ 1·0453,

$d\frac{25^\circ}{25^\circ}$ 1·0415.

The magnetic rotation determinations gave—

	t.	Sp. rotation.	Mol. rotation.
	14·0°	1·1400	11·219
	14·4	1·1406	11·229
	14 8	1·1397	11·229
	13·0	1·1469	11·278
	13·5	1·1481	11·244
	13·5	1·1429	11·243
	14·0	1·1421	11·240
	22·5	1·1322	11·215
	22·0	1·1320	11·207
	21·5	1·1340	11·224
Average	16·3	1·1393	11·233

Methyl Mesaconate.

This was prepared by saturating a mixture of mesaconic acid and methyl alcohol with hydrochloric acid. The ether was washed with sodium carbonate. It boiled at 205·5—206·5° (corr.). The density determinations gave—

$d\frac{4°}{4°}$ 1·1360, $d\frac{15°}{15°}$ 1·1253,

$d\frac{10°}{10°}$ 1·1302, $d\frac{20°}{20°}$ 1·1207,

$d\frac{25°}{25°}$ 1·1170.

The determinations of the magnetic rotation gave—

	t.	Sp. rotation.	Mol. rotation.
	15·2°	1·1631	9·073
	14·3	1·1645	9·077
	14·0	1·1610	9 047
	14·0	1·1610	9·047
Average	14·4	1·1619	9·061

Mesityl Oxide. Methyl Isobutenyl Ketone.

The product examined was obtained from Kahlbaum. It was dried by means of anhydrous potassium carbonate, and repeatedly fractioned. The specimen selected boiled at 129·5—130° (corr.). The density determinations gave—

$d\frac{4^\circ}{4^\circ}$ 0·8706, $d\frac{15^\circ}{15^\circ}$ 0·8612,

$d\frac{25^\circ}{25^\circ}$ 0·8548.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
11·6°	1·2336	7·775
11·6	1·2366	7·794
11·6	1·2333	7·773
11·6	1·2333	7·773
Average 11·6	1·2342	7·778

Observations on the Results obtained with Saturated Compounds.

Malonic, Succinic, and Glutaric Compounds.

From previous experiments (Trans., 1884, 570) it appeared that succinic acid was the first member of the homologous series of the bibasic acids, though from analogy it was more probable that it should commence with glutaric acid. The results obtained from the examination of glutaric acid given in this paper show that the latter supposition is apparently correct, as its series constant is lower than that of ethyl succinate, thus :—

Molecular rotation of ethyl succinate	8·380
Less $CH_2 \times 8 = 1·023 \times 8$	8·184
Series constant	0·196
Molecular rotation of ethyl glutarate.....	9·356
Less $CH_2 \times 9 = 1·023 \times 9$	9·207
Series constant	0·149

Numbers obtained by a fresh examination of ethyl sebate give results a little lower than these previously obtained, these give a series constant very nearly the same as that of ethyl glutarate, thus—

Molecular rotation of ethyl sebate	14·459
Less $CH_2 \times 14 = 1·023 \times 14$.....	14·322
	0·137

The number previously obtained for the mol. rot. of ethyl sebate

was 14·496, if this be averaged with the new results it gives 14·477, and this has a series constant of 0·155, so that there can be no doubt that glutaric and sebacic acids are true members of the homologous series. It is quite probable that a re-examination of ethyl suberate would also give somewhat lower numbers than those previously obtained, and thus also would be found to have the correct series constant. The molecular rotation required for this substance would be 12·425, the number found was 12·461, and a very small error in reading would cause this, as the molecular weight of the ether is high.

The molecular rotation found for propyl succinate also gives a lower series constant than ethyl succinate, this is quite in accordance with other observations, the propyl-groups usually having this influence. The series constant is much the same as that of ethyl glutarate and sebate.

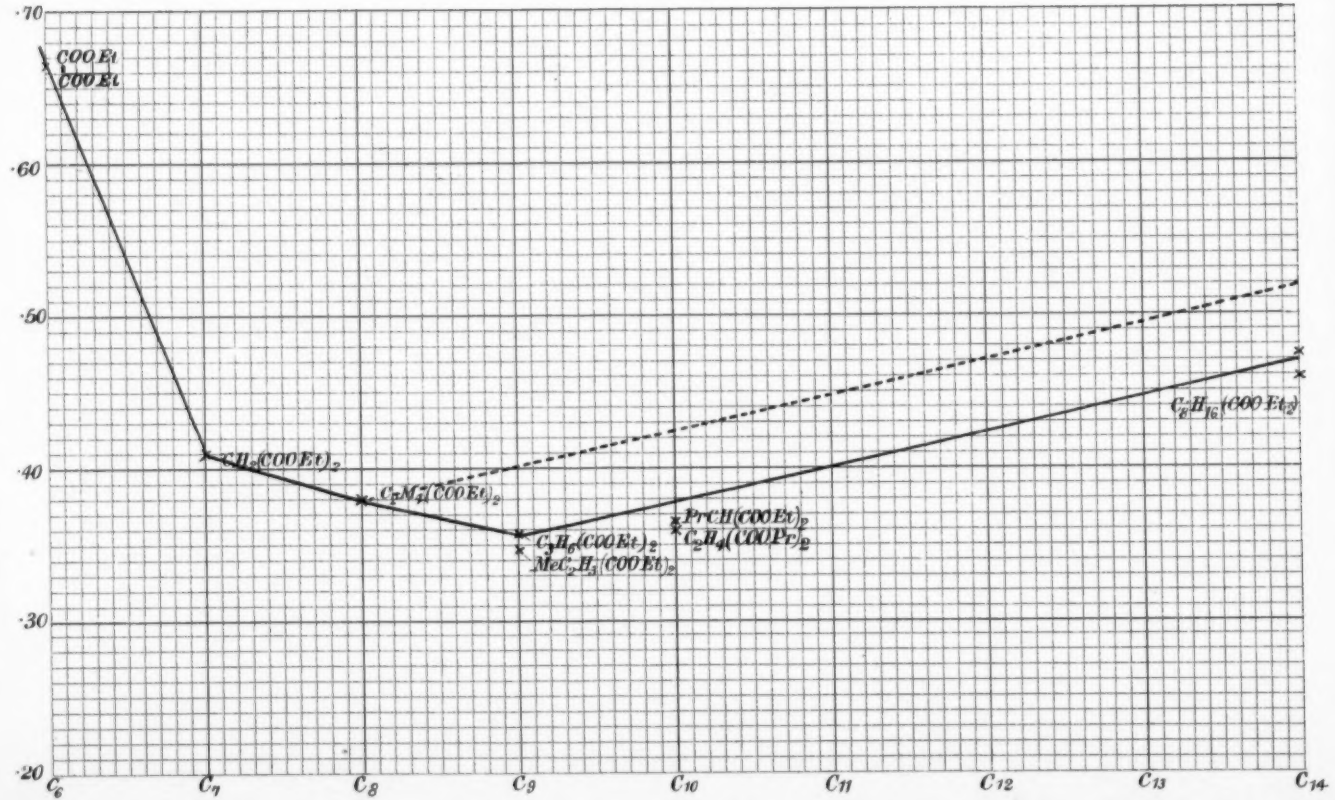
Molecular rotation of propyl succinate....	10·363
Less $CH_2 \times 10 = 1·023 \times 10$.....	10·230
	0·133

The molecular rotation of ethyl glutarate is nearly identical with methyl succinate (pyrotartarate) of ethyl, which is 9·347.

The accompanying diagram shows the relative position of the molecular rotations of the ethers of the bibasic acids, those of some of the isomeric compounds being also given. In the diagram in my previous paper, the homologous series was supposed to follow the direction which is indicated by the dotted line, this is now substituted by the line starting from ethyl glutarate, and following on to ethyl sebate.

It is interesting to notice that in the case of the monobasic acids and ethereal salts that the molecular rotation drops from formic to acetic acid and again, but in a less degree, to propionic acid, the true homologous series then commencing (see Diagram VI, Trans., 1884, 548). In the case of the ethers of bibasic acids, we get this peculiarity to a greater extent, the drop occurring three times before the true homologous series commences. (See accompanying diagram.)

The relationships of the magnetic rotations of the ethers of the bibasic acids to the acids themselves have hitherto been only inferred from the results obtained from the examination of the monobasic acids and of their ethereal salts; some experiments were therefore made in this direction, but as the bibasic acids are solid and not easily fusible, solutions had to be employed, this makes accurate results more difficult to obtain. Two of the most soluble acids were taken,



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namely, malonic and glutaric acids. Succinic acid was not considered to be sufficiently soluble.

The numbers obtained show the following relationships to the ethers :—

Ethyl malonate	7·410
Malonic acid	3·474
Diff. for replacement of H_2 by $(C_2H_5)_2$	3·936
Ethyl glutarate	9·356
Glutaric acid	5·482
Diff. for replacement of H_2 by $(C_2H_5)_2$	3·874

In the case of the fatty acids best comparable with these, we get—

Ethyl acetate	4·462	
Acetic acid	2·525	
Difference for replacement of H by C_2H_5	1·937	= for replacement of H_2 by $(C_2H_5)_2$ = 3·874.
Ethyl propionate	5·452	
Propionic acid	3·462	
Difference for replacement of H by C_2H_5	1·990	= for replacement of H_2 by $(C_2H_5)_2$ = 3·980.

These comparisons show that the influence of etherification in the case of the bibasic acids is very similar to that of the monobasic acids. These results, however, are not quite so consistent as might be expected, because the difference between the propionic and glutaric compounds and between the acetic and malonic compounds should compare, instead of which they are reversed; this, however, may be caused by some small error due to examining the malonic and glutaric acids in solution.

Pyrotartaric Anhydride.

The primary object in examining this compound was to compare it with the anhydrides of the unsaturated acids, as well as to study its rotation in reference to that of pyrotartaric acid itself. The latter relationship will be considered here, the former further on.

The rotation of pyrotartaric (methylsuccinic) acid has not been determined, but as its ether gives numbers nearly identical with those of ethyl glutarate, there can be no doubt its rotation is practically the same as that of glutaric acid.

Pyrotartaric acid (estimated).....	5·482
„ anhydride	4·750
	0·732

This number is about that which would be expected, and shows that this anhydride when uniting with water to form the acid gives a rotation which is *less* than the sum of the rotation of the anhydride plus the rotation of water; this agrees with all previous observations of saturated compounds when uniting with water to form new compounds.

Acetyl and Succinyl Chlorides.

Acetyl chloride was examined chiefly to get an idea of the value of chlorine in such compounds, as it was evident that by comparing it with aldehyde, the value of this element when replacing hydrogen could be obtained, thus :—

Acetyl chloride.....	3·800
Aldehyde.....	2·385
Influence of Cl replacing H.....	1·415
Value of H.....	0·254
Value of Cl.....	1·669

This is a little lower than the value of chlorine in propyl chloride, which is 1·733.

With respect to succinyl chloride, the only compound it can at present be compared with is ethyl succinate.

Ethyl succinate.....	8·380
Succinyl chloride	7·242
Difference	1·138

If a similar comparison be made with acetyl chloride and ethyl acetate, thus—

Ethyl acetate.....	4·463
Acetyl chloride.....	3·800
Difference	0·662 × 2 = 1·324

we get a result which is not very much more than half of that obtained with the succinic compound. At any rate it shows there must be a pretty close analogy between the rotation of the chlorides of acetyl and acetic compounds and the chlorides of succinyl and succinic

compounds. The above difference would at the same time indicate that the value of chlorine in succinyl chloride is slightly higher than in acetyl chloride.

Mesityl Oxide. Methyl Isobutenyl Ketone.

As no unsaturated ketone had been examined in reference to its magnetic rotation, I was anxious to know whether this substance would bear to analogous saturated compounds the usual relationship. As this is an iso-compound it is necessary to compare it with a saturated isoketone or allow for the influence of this group, the latter will be the simplest method; methyl butyl ketone has not been examined but methyl propyl ketone has, so that by adding the value of CH_2 to this the desired rotation will be found.

Molecular rotation of mesityl oxide	7·778
Methyl propyl ketone, 5·499 + 1·023	6·522
	1·256
Less influence of iso-group	0·111
	1·145

This is a difference only slightly in excess of that found to exist between ethyl α-crotonate and ethyl butyrate. This ketone therefore behaves in a manner similar to other unsaturated compounds as regards its magnetic rotation.

Maleic, Citraconic, and Itaconic Acids.

When considering the rotation of mesityl oxide, reference was made to the difference of rotation between saturated and unsaturated compounds, the latter having a larger rotation to the extent of a little more or less than 1·0, with the exception of allyl compounds, it has been found to be a little greater than 1·0 as in ethyl α-crotonate and ethyl oleate, where it is 1·112. The following is a comparison of the ethereal salts of maleic, citraconic, and itaconic acids with saturated acids:—

Ethyl maleate	9·625
Ethyl succinate	8·380
	1·245
Ethyl citraconate	10·517
Ethyl pyrotartarate	9·347
	1·170

Ethyl itaconate	10·467
Ethyl pyrotartarate	9·347
	1·120

In all these cases, the difference is only a little higher than 1·0, and these acids may therefore be regarded as ordinary unsaturated compounds related to succinic and pyrotartaric (methylsuccinic) acids in the same way as α-crotonic and oleic acids are to butyric and stearic acids.

The relationship of maleic and citraconic acids to their ethers is also analogous to that existing between the saturated monobasic and bibasic acid and their ethers, thus :—

Ethyl maleate	9·625
Maleic acid.....	5·633
Difference	3·992
Ethyl citraconate.....	10·517
Citraconic acid	6·567
Difference	3·950

It has been shown that in the case of malonic and glutaric acids and their ethers the differences are respectively 3·936 and 3·874, and with acetic and propionic acids 1·937 and 1·990 respectively, which multiplied by 2 give 3·874 and 3·980. These results go to show that in the formation of the ethers of these unsaturated acids the same kind of chemical change takes place as with the saturated acids, and therefore that they are of similar structure, that is, each acid contains two COOH groups.

The relationship of ethyl and methyl citraconate to each other is also analogous to that of ethyl and methyl succinate :—

Ethyl citraconate ...	10·517	Ethyl succinate	8·380
Methyl citraconate..	8·364	Methyl succinate	6·232
Difference.....	2·153	Difference.....	2·158

Fumaric and Mesaconic Acids.

From the magnetic rotation of the ethereal salts of these acids, they are evidently abnormal compounds, the numbers they give being remarkably high, nearly as high as would be given by an unsaturated compound differing from a saturated one by H_4, thus :—

Ethyl fumarate	10·116
Ethyl succinate	8·380
Difference	1·736
Ethyl mesaconate	11·233
Ethyl pyrotartarate.....	9·347
	1·886

It may be as well to notice here that the relationship of ethyl and methyl mesaconate is analogous to that of ethyl and methyl succinate:—

Ethyl mesaconate	11·233
Methyl mesaconate.....	9·061
	2·172

As shown previously, the difference in the case of the succinate is 2·158.

As bearing upon the general structure of fumaric acid, we may consider its chloride. The only comparison we have in this case is its relationship to its ether:—

Ethyl fumarate.....	10·116
Fumaryl chloride.....	8·747
	1·369

This is a little higher than the difference found between ethyl succinate and succinyl chloride, which is 1·138; but it is nearly the same as twice the difference found between ethyl acetate and acetyl chloride, which comes to 1·324. So that there is no reason to think that their structure, so far as the existence of carboxyl-groups is concerned, differs from that of ordinary acids. If, then, maleic and fumaric acids contain these groups, the cause of their isomerism must be related to the part of the acid they are attached to.

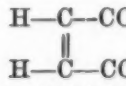
From the high magnetic rotation of fumaric acid, as well as its greater stability and smaller solubility than maleic acid, it is natural to infer that in the case of the former there is some kind of condensation or closer union between the molecules than in the latter, and I have previously brought this view forward (Trans., 1881, 560). This idea coincides to some extent with the views advanced by Kekulé, in which an explanation of the isomerism is sought in the idea of saturated and free affinities. If this, however, holds good, probably all unsaturated compounds, except fumaric and mesaconic acids and perhaps one or two others, would have to be regarded as

having free affinities, judging from the magnetic rotation of those already examined. But this idea of condensation or closer union of the molecules in fumaric and mesaconic acids is negatived by some of the physical properties of these substances. If it existed, we should expect that the ethereal salts of these compounds would have higher boiling points and greater densities than those of maleic and citraconic acids. The following comparison shows how they stand to each other:—

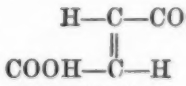
Ethyl maleate, b. p.	225·0°	$d\frac{15°}{15°}$ 1·0740
Ethyl fumarate, „	218·5°	„ 1·0623
	6·5°	0·0017
Ethyl citraconate, b. p.....	230·3°	$d\frac{15°}{15°}$ 1·04€8
Ethyl mesaconate, „	228·0°	„ 1·0492
	2·3°	+ 0·0024

Ethyl itaconate boils at 227·8°, and has a density of $d\frac{15°}{15°}$ 1·0504, so that we find the boiling points of ethyl maleate, citraconate, and itaconate are actually *higher* than those of ethyl fumarate and mesaconate. The densities of ethyl maleate and itaconate are also *higher* than those of these ethers, that of the citraconate being, however, a trifle lower than that of the mesaconate.

No doubt the most striking peculiarity of fumaric and mesaconic acids is their apparent inability to form anhydrides, and in this respect they resemble terephthalic acid; maleic, citraconic, and itaconic acids behave like phthalic acid, which easily gives an anhydride. The isomerism between phthalic acid and terephthalic acid being due to difference of position, can such an explanation be used in reference to the compounds under consideration? Van't Hoff, I believe, was the first to suggest this view. The difference of position in these compounds can be represented either by his figure, or on a plane by assuming the existence of a two-carbon chain. Taking maleic and fumaric acids as instances, we get—



Maleic acid.

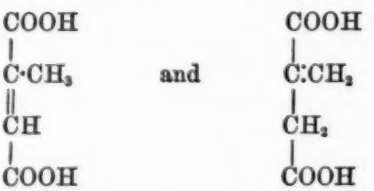


Fumaric acid.

In this way, maleic, citraconic, and itaconic acids would most resemble ortho-compounds, and fumaric and mesaconic acids para-

compounds; but if this be so, are these differences of position likely to cause the ethers of the latter acids to give larger magnetic rotation than those of the former? This is difficult to answer at present. Difference of position in the aromatic series does affect the magnetic rotation of bodies very considerably, and I may mention that I have examined the ethers of phthalic and isophthalic acids, and find that the latter gives a slightly *higher* rotation than the former, but the difference is very small. The more correct comparison, however, would most probably be between phthalic and terephthalic acids. The latter I hope to measure before long. At the present moment, the position theory appears to afford the best means of explaining the isomerism of these unsaturated acids.

As to the difference of constitution of citraconic and itaconic acids, the magnetic rotation does not give much light. If they be represented thus—



the difference will be in reference to displacements by CH_3— and $CH_2{=}$, and we have no perfectly parallel cases examined as regards the influence such displacements would have on the magnetic rotation of substances. The only comparisons we have which are near to this are between the ethereal salts of succinic and methylmalonic acid and those of pyrotartaric and glutaric acids. In the former, the rotation varies by 0·05, and in the latter by only 0·01, the lower rotations being for the methyl replacements. The rotation of ethyl itaconate is 0·05 lower than that of the citraconate, so that, if anything, these comparisons would be in favour of itaconic acid containing methyl.

The boiling points of the ethereal salts of methylmalonic and pyrotartaric acids are a good deal lower than those of the ordinary succinic and glutaric acids. The boiling point of ethyl itaconate is also lower than that of ethyl citraconate, but only about 2·5°.

A number of experiments were made on the oxidation of citraconic, mesaconic, and itaconic acids with chromic mixture and by fusion with alkali, but they all gave acetic acid; in the case of citraconic acid, when fused with alkali, the silver salt prepared from the distilled acid gave numbers indicating the presence of propionic acid in small quantities.

The oxidation of these acids with permanganate takes place with different degrees of rapidity. Thus when a small quantity is added to

a dilute solution of citraconic acid slightly acidified with sulphuric acid, the colour disappears after about 15 seconds, whilst with exactly similar solutions of mesaconic and itaconic acids the colour vanishes almost immediately. With alkaline permanganate, moreover, these acids do not behave in the same way; thus, with dilute alkaline solutions of the three acids made exactly alike, the alkaline permanganate does not become green with the citraconic solution until about 20 seconds have elapsed, it then slowly becomes turbid; the mesaconic solution becomes green at once, and then gradually opaque and greenish-yellow; whilst the itaconic solution becomes green at once, and remains bright. These three acids when thoroughly oxidised with alkaline permanganate yield oxalic acid; no acetic acid was found.

Maleic and Citraconic Anhydrides.

These anhydrides were measured in different ways. Maleic anhydride being solid was examined in solution only, and citraconic both in the pure state and dissolved. From the examination of the latter in the pure state, there can be no doubt about its rotation, but when dealing with solutions of these anhydrides in different solvents, it is necessary to bear in mind that they are unsaturated compounds, and may combine more or less with the solvents, and produce saturated compounds, therefore when doing those of maleic anhydride in acetic acid or acetic anhydride, corresponding experiments were always made with citraconic anhydride and these solvents, because the true value of this compound had been obtained with the pure substance. It was found that these solvents did slightly alter the rotation of citraconic anhydride, and at last citraconic anhydride itself was used as the solvent for maleic anhydride, as these two compounds being of the same kind and so nearly related, were not likely to influence each other. The following are the results obtained:—

I.

Rotation obtained for maleic anhydride in acetic acid	4·448
Maleic anhydride in acetic anhydride	4·417
Maleic anhydride in citraconic anhydride	4·545

II.

Citraconic anhydride in acetic acid.....	5·448
Citraconic anhydride in acetic anhydride	5·488
Citraconic anhydride alone	5·540

so that the solutions in Series I give numbers about 0·10—0·13 lower than do the mixture of maleic anhydride and citraconic

anhydride. In Series II they are from 0·052—0·092 lower than those given by pure citraconic anhydride.

Density determinations were made with the solutions of maleic and citraconic anhydride in acetic anhydride from 10° to 100°, thinking that they might throw some light on the cause of the small difference of rotation, but they do not give any definite evidence on the subject. It was, however, thought best to give the determinations, as they may be useful for future reference.

There can be no reason to doubt, however, that the magnetic rotation obtained for maleic anhydride when determined in its solution in citraconic anhydride is practically correct, and this is borne out by the following comparisons of this substance, and citraconic anhydride with their respective ethers, with which they show practically the same difference :—

Ethyl maleate	9·625	Ethyl citraconate ...	10·517
Maleïc anhydride	4·545	Citraconic anhydride	5·540
Difference	5·080	Difference	5·077

In previous papers I have drawn attention to the fact, that when water unites with a substance so as to produce a new product, the rotation of the latter is less than the sum of the rotations of water and the substance with which it has chemically united, but in the case of maleic and citraconic anhydrides, when they unite with water to form their respective acids, we get the extraordinary result that the acids possess rotations actually *greater* than the sum of the rotation of the anhydrides and the water they have united with.

Maleic acid	5·633	Citraconic acid	6·567
Maleic anhydride	4·545	Citraconic anhydride .	5·540
OH_2	1·088	OH_2	1·027

Now if the water had been present even in an uncombined way its value would have been only 1·000, and yet there is no doubt that in this case its union with the anhydrides has resulted in the formation of new compounds. As no anhydrides of the bibasic acids had been examined, the experiments on pyrotartaric anhydride already given were made (p. 565) to see whether it behaved in a normal or abnormal manner when hydrated. From the comparisons already given, it is seen that the difference between the rotation of this anhydride and its acid is only 0·732, or considerably less than 1·000, a result consistent with all previous observations.

Citraconic anhydride behaves as an unsaturated compound, giving

a rotation which is considerably higher than the corresponding saturated anhydride thus:—

Citraconic anhydride	5·540
Pyrotartaric anhydride.....	4·764
	0·776

but this difference is much smaller than that existing between most unsaturated compounds, especially those related to it, which give from 1·120 to 1·245, as already shown. This peculiarity of the rotations of maleic and citraconic anhydrides leads to the inference that there is something anomalous in their constitution, or that when in the fluid condition they do not consist of simple molecules of the formulæ $C_4H_2O_3$ and $C_5H_4O_3$, but of those with more complex ones formed by one molecule saturating another, and thus reducing the rotation (when in the state of vapour, maleic anhydride has the ordinary formula: Hübner and Schrieber, *Z.*, 1871, 713). Some experiments were therefore made with citraconic anhydride, to see, if such molecules existed, whether they would break up on heating. The magnetic rotation determinations of this substance were made along with comparable ones of pyrotartaric anhydride, because it is found that the molecular rotation of a substance is not quite constant for all temperatures, falling off a little with rise of temperature; this matter is at present occupying my attention. The numbers obtained were—

Citraconic anhydride at 17·4°	5·540
Citraconic anhydride at 65·7°	5·473
	0·077
Pyrotartaric anhydride at 11·6°	4·764
Pyrotartaric anhydride at 50°.....	4·737
	0·027

The citraconic anhydride determinations at high temperature show us a difference slightly in excess of those of the pyrotartaric anhydride; this would favour the idea of dissociation taking place to a very slight extent, but the variation is almost within the errors of experiment, and cannot be taken as any evidence of this. A large number of density determinations of citraconic anhydride were also made from 0—100° (p. 577), but it was found that these change in a very regular manner with the temperature, and within this range do not indicate dissociation. Endeavours were made to take the density of this substance at its boiling point, and also at the boiling point of aniline,

but in both cases decomposition with evolution of gas gradually took place, and rendered it impossible to do this.

The method of determining molecular weights proposed by Raoult was brought under my notice, and I have applied it to the determination of the molecular weight of these anhydrides and most of the substances referred to in this paper. The solvent used was glacial acetic acid, and the proportions of the substance used varied from about 1·4 to 1·6 to 100 of acid.

The following results were obtained :—

Substance.	Mol. wt. found.	Mol. wt. calculated.	Difference.
Citraconic acid	134·4	130	+4·4
Itaconic acid	134·8	130	4·8
Mesaconic acid	134·2	130	4·2
Ethyl citraconate	189·9	186	3·9
Ethyl itaconate	188·7	186	2·1
Ethyl mesaconate	187·7	186	1·1
Ethyl succinate	180·6	174	6·6
Ethyl maleate	179·1	172	7·1
Ethyl fumarate	177·3	172	5·3
Succinic anhydride	115·4	100	15·4
Pyrotartaric anhydride	131·2	114	17·2
Maleic anhydride	108·9	98	10·9
Citraconic anhydride	129·8	112	18·6

From the results of this method of determining the molecular weight, it appears that all the above acids and ethers have the molecular weight usually assigned to them, the variation in the number being but small and probably due to experimental errors. In the case of the anhydrides, however, the variations are somewhat larger and moderately consistent, and therefore probably not due to errors of experiment, but as both saturated and unsaturated anhydrides behave in the same way, their molecular conditions would appear to be the same, so that these results afford no help in explaining the peculiarities of the magnetic rotation of maleic and citraconic anhydrides. So far the evidence of the magnetic rotation of citraconic anhydride at high temperatures, the density determination through the range of temperature 0° to 100°, and Raoult's method of determining molecular weights, all give evidence against the existence of complex molecules. It may be there is some peculiarity in the constitution of these bodies we are not acquainted with; if so, it is difficult to conceive what it can be. I have been struck, however, with the peculiar behaviour of these anhydrides towards tertiary amines

with which we should not expect them to react easily. For example, if citraconic anhydride be added to triethylamine action sets in with great energy, the product becomes brown and strongly heated, and a brown pitch results which is partially soluble in water and partially insoluble. Maleic anhydride acts similarly. Citraconic anhydride also reacts with picoline, but not so freely as with triethylamine. Succinic anhydride does not behave in the same way with these bases; but whether the greater chemical activity of these unsaturated anhydrides is due to their being unsaturated compounds or to difference in structure from ordinary anhydrides, we have no means of proving at present; any explanation of their peculiar magnetic rotations, therefore, must be allowed to stand until more compounds of this class have been obtained and examined. Our knowledge of unsaturated compounds and their physical characteristics is at present very incomplete, that they are very different from those of saturated compounds the following instances in relation to boiling points will show:—

Saturated Compounds.

Ethyl succinate,	b. p.	216·5°	+34·5.
Succinic anhydride,	„	250·0	
Ethyl pyrotartarate,	„	218·0	+29·4.
Pyrotartaric anhydride,	„	247·0	

Unsaturated Compounds.

Ethyl maleate,	b. p.....	225°	−25.
Maleic anhydride,	„	200	
Ethyl citraconate,	„	230	−17.
Citraconic anhydride,	„	213	

The anhydrides in the case of the saturated compounds boil much higher than the ethers, but in unsaturated anhydrides boil considerably lower than the ethers.

The chief conclusions resulting from this inquiry may be briefly summarised:—

1. That glutaric acid appears to be the first true member of the homologous series of bibasic acids.

2. That the propyl ether of succinic acid has a lower series constant than the ethylic ether, a result which is consistent with analogous observations on some of the compounds of the fatty acids.

3. That pyrotartaric anhydride has a rotation which shows that when it unites with water condensation takes place as with other anhydrides, the rotation of the resulting acid being less than the sum of the rotation of the anhydride plus the rotation of water.

4. That the rotation of mesityl oxide shows that unsaturated ketones have rotations consistent with those of other unsaturated bodies.

5. That the ethereal salts of maleic, citraconic, and itaconic acids have rotations consistent with those of other unsaturated compounds differing from the saturated ones by H_2, and that their general structure appears to be analogous to that of ordinary bibasic acids.

6. That the ethereal salts of fumaric and mesaconic acids have much higher rotations than ordinary unsaturated compounds, being nearly sufficiently high for those represented by saturated compounds less H_4, and that their general structure is apparently analogous to that of ordinary bibasic acids, and that this difference of character to their isomers is apparently best accounted for by difference of position, *i.e.*, by the Vant' Hoff hypothesis.

7. That the rotations of maleic and citraconic anhydrides are abnormally low, and the reason for this cannot at present be satisfactorily explained.

8. That from the determinations by Raoult's method of the molecular weights of most of the substances examined in this paper, they seem to have the molecular weights usually ascribed to them—at any rate none appear to be polymers.

The following table gives a list of the substances which have been subjected to examination, with their molecular rotations and the pages where they are referred to.

	Molecular rotation.	Page.
Acids.		
Citraconic	6·567	580, 591, 595, 599.
Glutaric	5·482	566, 589, 600.
Maleic	5·633	572, 591–593.
Malonic	3·474	562, 589.
Ethers.		
Ethyl citraconate	10·517	581, 591, 592, 594, 599, 601.
Ethyl fumarate	10·112	574, 593, 594, 599, 601.
Ethyl glutarate	9·356	567, 587.
Ethyl itaconate	10·467	584, 592, 594, 599, 601.
Ethyl maleate	9·625	572, 591, 594, 599–601.
Ethyl sebate	14·459	568, 587.
Ethyl mesaconate	11·233	585, 593, 594, 599–601.
Methyl citraconate	8·364	583, 592, 600.
Methyl mesaconate	9·061	586, 593, 599, 601.
Propyl succinate	10·363	562, 588, 600.
Anhydrides.		
Citraconic	5·540	576, 596–601.
Maleic	4·548	568, 596–601.
Pyrotartaric	4·764	564, 589, 598–600.

	Molecular rotation.	Page.
Chlorides.		
Acetyl	3·800	590, 593.
Fumaryl	8·747	575, 593.
Succinyl	7·242	563, 590.
Ketone.		
Mesityl oxide	7·778	587, 591, 601.

XLIV.—*Oxidation of Oxalic Acid by Potassium Dichromate.*

By Emil A. Werner, F.I.C., Assistant in the Chemical Laboratory, Trinity College, University of Dublin.

In a preliminary notice on the above subject (Abstr., December, 1887), I pointed out that the oxidation of oxalic acid by potassium dichromate was limited by the formation of a chromoxalate, even in presence of sulphuric acid, provided the latter was not present in a concentrated form.

In the present paper, I propose to give the results of a study of the oxidation of oxalic acid by potassium dichromate, *per se*, and in varying molecular proportions. A paper on the same subject has been quite recently communicated to the Society by Mr. C. H. Bothamley (this vol., p. 159), but as the writer has overlooked the formation of a chromoxalate in the interactions, I believe that he has been misled in the interpretation of his results.

In short, for a complete and successful solution of the problems presented in the interactions of oxalic acid and potassium dichromate, a previous knowledge of the properties of the chromoxalates is absolutely necessary, more particularly of Croft's red potassium compound, whose precise composition and relations I have recently studied (this vol., p. 404).

Whether in the solid state, or in aqueous solution, 7 mols. of oxalic acid are required for the complete reduction of 1 mol. of potassium dichromate, the *sole* products of the interaction being Croft's salt, carbonic anhydride, and water, thus:—

$$K_2Cr_2O_7 + 7(H_2C_2O_4,2H_2O) = K_2H_2Cr_2(C_2O_4)_4(OH)_2 + 6CO_2 + 19H_2O.$$

The experimental data proving the correctness of this equation are given under Experiment I, further on.

Bearing in mind this equation, it seemed highly probable that all cases of the interaction of potassium dichromate and oxalic acid, between 1 and 7 mols., might be represented by one general equation, and the outcome of the present investigation has been to give complete corroboration to this view, and to prove that when dichromate on the one hand, or oxalic acid on the other, is used in excess beyond the proportions required by the foregoing equation, that excess is found in the residue on completion of the reaction.

The general method adopted in the experiments was the following:—An intimate mixture of the two substances, both in fine powder, was slowly heated in a dry, weighed, conical flask to the temperature of interaction, after which the flask with its contents was heated in an air oven at 110—120°, until the weight was constant, and the loss determined. This does not represent, as Mr. Bothamley assumed, "the *complete* dehydration of the oxalic acid and its partial oxidation by the dichromate," but its partial oxidation together with its *partial* dehydration, for the red potassium chromoxalate formed (*not chromic oxalate*) retains, as I have shown (Trans., 1888, 404), 2 mols. H_2O, at the temperature and under the conditions of the interaction. The residue was dissolved in water, diluted to a definite volume, and the chromium and oxalic acid determined in aliquot portions. The estimations of the carbonic anhydride by absorption in ammoniacal calcic chloride solution were made in separate experiments carried out in presence of water; the spontaneous nature of the reaction, accompanied as it is by considerable development of heat when the substances interact in the solid state, rendering the correct estimation of the carbonic anhydride by any absorption method very difficult.

The potassium dichromate and oxalic acid used in these experiments were both purified by recrystallisation, the latter carefully air-dried, whilst the former was heated to 150—160°, and allowed to cool in a desiccator.

A. *Potassium Dichromate* (1 *mol.*), *Hydrated Oxalic Acid* (7 *mols.*)

In this case the dichromate is completely reduced, and the interaction takes place according to the equation already given.

Expt. I.—5·1895 grams $\begin{cases} = 1{\cdot}2973 \text{ gram } K_2Cr_2O_7 \\ = 3{\cdot}8922 \text{ ,, } H_2C_2O_4,2H_2O. \end{cases}$

Temperature of interaction, 28—30°.

At 110—120°—

Loss	2·6445 grams	= 50·95	per cent. of total weight.
Theory ..	2·6741 ,,	= 51·53	,, ,,

$H_2C_2O_4,2H_2O$ (unoxidised as chromoxalate in residue)—

			Acid taken.		Acid unoxidised.
Found..	2·2570 grams.	Ratio..	100	:	57·98 or 7 : 4·05.
Theory..	2·2241 „	Ratio..	100	:	57·14 or 7 : 4.

The residue when dissolved in water yields a rich purple-red solution, perfectly free from any unaltered dichromate.

A series of experiments had previously shown that water, in whatever proportion it may be present, is entirely without influence on the nature of the interaction.

B. *Potassium Dichromate and Hydrated Oxalic Acid, equal Molecules.*

In this case, as the experimental results show, only one-seventh of the dichromate is reduced, six-sevenths remaining unaltered.

Expt. II.—5·5965 grams $\begin{cases} = 1\ 6789 \text{ gram } H_2C_2O_4,2H_2O. \\ = 3·9176 \text{ grams } K_2Cr_2O_7. \end{cases}$

Temperature of interaction, 30—32°.

At 110—120°—

Loss ..... 1·184 gram = 21·15 per cent. of total weight.
Theory .... 1·153 „ = 20·61 „ „

Cr_2O_3 formed—

			$K_2Cr_2O_7$ taken.		$K_2Cr_2O_7$ reduced.
Found..	0·297 gram = 0·5744 $K_2Cr_2O_7$		100	:	14·66 or 7 : 1·02.
Theory.	0·289 „ = 0·559 „		100	:	14·26 or 7 : 1.

$H_2C_2O_4,2H_2O$ (unoxidised, as chromoxalate)—

			Acid taken.		Acid unoxidised.
Found..	0·9610 gram.	Ratio..	100	:	57·23 or 7 : 4·006.
Theory.	0·9593 „	Ratio..	100	:	57·14 or 7 : 4.

Expt. III.—In presence of water, 5·9335 grams .... $\begin{cases} = 1·78 \text{ gram } H_2C_2O_4,2H_2O. \\ = 4·1535 \text{ „ } K_2Cr_2O_7. \end{cases}$

CO_2 evolved—

Found .. 0·553 gram = 0·7917 gram $H_2C_2O_4,2H_2O$.
Theory.. 0·5327 „ = 0·7628 „ „

Cr_2O_3 formed—

		$K_2Cr_2O_7$ taken.		$K_2Cr_2O_7$ reduced.
Found ..	0·3110 gram	7	:	1.
Theory..	0·3067 „			

$H_2C_2O_4,2H_2O$ (unoxidised)—

Found ..... 1·032 gram.
Theory ..... 1·0171 „

C. *Potassium Dichromate* (1 *mol.*), *Hydrated Oxalic Acid* (2 *mols.*).

In this case, $\frac{3}{7}$ of the dichromate are reduced, $\frac{5}{7}$ remaining unaltered.

Expt. IV.—5·3805 grams { = 2·4833 grams $H_2C_2O_4$, $2H_2O$. = 2·8972 „ $K_2Cr_2O_7$.

Temperature of interaction, 51—52°.

At 110—120°— Loss.... 1·726 gram = 32·07 per cent.
Theory.. 1·706 „ = 31·71 „

Cr_2O_3 formed— Found .. 0·432 gram.
Theory.. 0·429 „

$H_2C_2O_4,2H_2O$ (unoxidised)—
Found .... 1·421 gram. Theory.... 1·419 gram.

Expt. V.—5·66 grams in presence of water.
CO_2 evolved—
Found .. 0·7933 gram = 1·1358 gram $H_2C_2O_4,2H_2O$.
Theory.. 0·7819 „ = 1·1195 „ „

D. *Potassium Dichromate* (1 *mol.*), *Hydrated Oxalic Acid* (9 *mols.*), *corresponding to* $K_2Cr_2O_7 + 7 + 2$ mols. $H_2C_2O_4,2H_2O$.

In this case, the interaction takes place as in A, the excess of oxalic acid over the 7 mols. remaining unaltered.*

Expt. VI.—5·64 grams in presence of water .. { = 4·479 grams $H_2C_2O_4,2H_2O$. = 1·161 „ $K_2Cr_2O_7$.

CO_2 evolved— Found .. 1·110 gram.
Theory.. 1·042 „

Cr_2O_3 formed— Found .. 0·621 gram.
Theory.. 0·600 „

$H_2C_2O_4,2H_2O$ (unoxidised)—

		Acid taken.		Acid unoxidised.
Found	3·003 grams	9	:	6·03
Theory....	2·986 „	9	:	6·00

* In this particular case, the excess of oxalic acid combines with the red chromoxalate, forming the feeble compound $K_2H_4Cr_2(C_2O_4)_6$ of the blue series, which, however, is decomposed by much water.

Solutions prepared directly from potassium dichromate and red potassium chromoxalate in the proper proportions, were found in each case to be identical in every respect with the solutions of the products of the respective interactions.

With anhydrous oxalic acid, the interactions are the same as with the hydrated acid, with the exception that *anhydrous* chromoxalate is formed as the following experiments show.

Expt. VII.—Potassium Dichromate and Anhydrous Oxalic Acid equal mols. 4·9645 grams. Temperature of interaction, 40—42°.

Loss....	0·7675 gram	= 15·45 per cent.
Theory for hydrated chromoxalate		= 13·16 „
„ anhydrous „		= 14·50 „

Expt. VIII.—Potassium Dichromate (1 *mol.*) *Anhydrous Oxalic Acid* (2 *mols.*). 5·28 grams. Temperature of interaction, 54—56°.

Loss....	1·291 gram	= 24·45 per cent.
Theory for hydrated chromoxalate		= 21·33 „
„ anhydrous „		= 23·50 „

The rather high result obtained in each case is due to a loss of a small quantity of the oxalic acid by sublimation. The residue from the interaction presents the appearance of a light, bulky, porous, pale-brown mass, which develops heat when moistened with water.

From a study of the interaction of *equal* weights of potassium dichromate and hydrated oxalic acid, Mr. Bothamley deduced the following equation, as representing the change which takes place at 110—120°, viz.:—

$$2K_2Cr_2O_7 + 6H_2C_2O_4 = Cr_2(C_2O_4)_3 + 6CO_2 + 6H_2O + 2K_2CrO_4.$$

As I have already mentioned, chromic oxalate is not formed in any of these decompositions, and neutral potassium chromate is never present as a product of the interaction of potassium dichromate and oxalic acid below 200° under any conditions.

The equation adopted by Mr. Bothamley agrees only approximately with his experimental results, and, moreover, it does not represent the molecular ratios with which he worked.

Equal weights of potassium dichromate and hydrated oxalic acid, correspond exactly with the molecular ratios:—

$3K_2Cr_2O_7$	882
$7(H_2C_2O_4,2H_2O)$	882,

therefore 2 mols. of dichromate will be left unchanged, according to the equation—

$$3K_2Cr_2O_7 + 7(H_2C_2O_4,2H_2O) = K_2H_2Cr_2(C_2O_4)_4(OH)_2 + 2K_2Cr_2O_7 + 6CO_2 + 19H_2O,$$

and this is proved by the following experiments.

E. *Potassium Dichromate and Hydrated Oxalic Acid, equal weights.*

Expt. IX.—5·73 grams (= 2·865 grams $H_2C_2O_4,2H_2O$). Temperature of interaction, 32—35°.

Loss	1·9395 grams	= 33·84 per cent.
Theory	1·9684 „	= 34·29 „

Cr_2O_3 formed—

Found .. 0·503 gram. Theory .. 0·4937 gram.

$H_2C_2O_4,2H_2O$ (unoxidised)—

Found .. 1·662 gram. Theory .. 1·637 gram.

Expt. X.—Same as above, in presence of water. 5·875 grams.

CO_2 evolved—

Found.. 0·9022 gram. Theory.. 0·8792 gram.

Mr. Bothamley's own results agree fairly well with the above equation: thus he obtained in two experiments the numbers 100 : 54 and 100 : 53 for the ratios of oxalic acid, taken to oxalic acid unoxidised, from which he concluded that half of the acid was oxidised, but the true ratio is 100 : 57 or simply 7 : 4. The absence of neutral potassium chromate in the products from any one of the preceding interactions is readily proved by the absence of any *immediate* precipitate on the addition of barium chloride or nitrate solutions to the product.

Mr. Bothamley states (referring to the solution of the product from the interaction of the dichromate and oxalic acid, in equal weights) that when mixed with ammonia, a brown precipitate of chromium chromate is formed; in my experiments, ammonia did not produce a trace of precipitate, but simply a change in colour, due to its action on the red potassium chromoxalate present.

The interactions of potassium dichromate and oxalic acid at a low red heat vary considerably with the proportions of dichromate and red chromoxalate forming the mixture, and though the decompositions are very simple, yet they require rather complex equations for their representation. The fact is, that the changes which occur under this condition are the result of the ordinary decomposition of the potassium chromoxalate complicated by the exceptional oxidising action of the dichromate on the oxalic radicle of the latter.

In the second part of my paper on the chromoxalates (Trans., 1888,

404), I have shown that the red potassium salt* decomposes at a red heat in accordance with the equation—

$$2K_2H_2Cr_2(C_2O_4)_4(OH)_2 + 11O = 2K_2CrO_4 + Cr_2O_3 + 16CO_2 + 4H_2O.$$

In the present cases, the oxygen necessary for the decomposition is wholly derived from the dichromate (which is reduced correspondingly) when the latter is in excess, whilst if the chromoxalate is in excess, the whole of the dichromate is reduced (to Cr_2O_3 and K_2CrO_4), the remainder of the oxygen being derived from the air. As this interaction is of secondary interest as compared with the more important primary change, I merely give the following two cases as examples:—

F. *Product from Interaction of* $K_2Cr_2O_7$ *and Hydrated Oxalic Acid, equal mols.*

$$\text{Ratio} = \begin{cases} 1K_2H_2Cr_2(C_2O_4)_4(OH)_2. & \text{(See } \textit{Expt. II}\text{, B).} \\ 6K_2Cr_2O_7. \end{cases}$$

Equation:

$$36K_2Cr_2O_7 + 6K_2H_2Cr_2(C_2O_4)_4(OH)_2 = 14Cr_2O_3 + 14K_2Cr_2O_7 + 28K_2CrO_4 + 48CO_2 + 12H_2O.$$

Expt. XI.—0·944 gram. Heated to a low red heat. Decomposition without violence.

Residue—	Found ..	0·7900 gram	= 83·68 per cent.
	Theory..	0·787 „	= 83·37 „

Cr_2O_3 formed—

Found .. 0·1485 gram. Theory .. 0·1434 gram.

G. *Product from Interaction of* $K_2Cr_2O_7$ *and* $H_2C_2O_4,2H_2O$, *equal weights.*

$$\text{Ratio} = \begin{cases} 1K_2H_2Cr_2(C_2O_4)_4(OH)_2. & \text{(See } \textit{Expt. IX}\text{, E).} \\ 2K_2Cr_2O_7. \end{cases}$$

Equation:

$$4K_2Cr_2O_7 + 2K_2H_2Cr_2(C_2O_4)_4(OH)_2 + 5O = 3Cr_2O_3 + 6K_2CrO_4 + 16CO_2 + 4H_2O.$$

Expt. XII.—0·6175 gram. Heated to low red heat. Decomposition violent.

Residue—	Found ..	0·4300 gram	= 69·63 per cent.
	Theory..	0·4318 „	= 69·94 „

* Omitting the water of crystallisation.

Cr_2O_3 formed—

Found .. 0·1155 gram. Theory .. 0·1215 gram.

Comparative experiments, made with an intimate mixture prepared directly from finely-powdered dichromate and red potassium chromoxalate in the proper proportions, led to the same results.

It is noteworthy that the mixed solution of potassium dichromate and red chromoxalate which results from the preceding interactions, or a directly prepared solution of the two salts, though exhibiting in every respect the properties of its constituents, refuses to crystallise under the most favourable conditions. The absorption spectrum of the mixed solution was found from a preliminary examination to be the sum of the absorption-spectra of the solutions of the separate constituents. The two compounds appear to exist in a feeble state of molecular combination just sufficient to prevent either one or the other from crystallising out. I hope to examine the solution further, later on.

The results of the present investigation may be summed up in the following conclusions:—

1. The red potassium chromoxalate, $K_2H_2Cr_2(C_2O_4)_4(OH)_2$ (Croft's salt), is in all cases, *without exception*, a product of the interaction of potassium dichromate and hydrated oxalic acid, below 200°.
2. Neutral potassium chromate is *never* present as a product of the interaction of potassium dichromate and oxalic acid under any conditions below 200°.
3. When the two substances interact in the solid state, the initial temperature of the interaction, which lies between 30° and 60°, varies with the molecular proportions employed.
4. The dehydration of the oxalic acid does not affect the nature of the interaction, the anhydrous chromoxalate, $K_2Cr_2(C_2O_4)_4$, being formed in this case.
5. Water, by its solvent action, facilitates the interaction, that is, reduces the initial temperature, but is otherwise without influence on the nature of the change.
6. Seven mols. of oxalic acid is the *minimum* quantity necessary for the complete reduction of 1 mol. of potassium dichromate, and any *excess of* either above this ratio remains unchanged.
7. When the proportion of potassium dichromate to oxalic acid exceeds 1 to 7 mols., and the temperature of the mixture is raised to low redness, a secondary reaction occurs between the excess of dichromate and the red chromoxalate first formed.

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XLV.—*The Determination of the Molecular Weights of the Carbohydrates.*

By Horace T. Brown and G. Harris Morris, Ph.D.

But very little is known with certainty, at the present time, about the true molecular composition of the majority of the carbohydrates. The vapour-density method is obviously inapplicable to them, and chemists have had, for the most part, to be satisfied with a determination of the *minimum* size of their molecules, from a study of their somewhat indefinite metallic derivatives, and of their acetyl-compounds.

Musculus and Meyer (*Bull. Soc. Chim.* [2], **35**, 370) have attempted to determine the relative size of the molecules by observing the rate of diffusion of the different members of the group, but, although the results are of interest, they do not go far in determining the particular point we have before us.

In the case of *dextrose* and *levulose*, there is a considerable amount of positive evidence that their molecular composition is expressed by the formula $C_6H_{12}O_6$. This is shown by their intimate relation to the hexahydric alcohol *mannitol*, and by the recent researches of Kiliani on their cyanhydrins, which yield hydroxy-acids containing seven atoms of carbon.

With regard to the higher carbohydrates, the knowledge we possess as to their molecular weight is entirely indirect. In the case of *starch* and the *dextrins*, we are quite sure, from the way in which they break up under the action of diastase and dilute acid, that their molecular structure must be very complex, and we are able to learn something about the *relative* size of the molecules, but that is all.

Within the last few weeks, Victor Meyer (*Ber.*, 1888, 556) and Auwers (*Ber.*, 1888, 860) have directed attention to a new method for determining molecular weights, which is applicable to all organic substances, and is of special value where a determination of vapour-density is impossible. This method was devised by Raoult (*Ann. Chim. Phys.* [5], **28**, 133, 1883; *id.* [6], **2**, 66—124, 1884; *id.* [6], **4**, 401, 1885; *id.* [6], **8**, 289 and 317, 1886; *Compt. rend.*, **94**, 1517, 1882; **101**, 1056, 1885; **102**, 1307, 1886), and is the outcome of his elaborate investigation into the laws governing the freezing point of dilute solutions, and it is certainly a remarkable fact that these important researches should, up to recently, have received so small a share of attention from chemists.

Blagden, as early as 1788 (*Phil. Trans.*, **78**, 277), established the fact, with regard to inorganic salts, that the lowering of the freezing point of their aqueous solutions is proportional to the weight of substance dissolved in a constant weight of water. De Coppet (*Ann. Chim. Phys.* [4], **23**, 25—26), in 1871–72, clearly pointed out that when this lowering of the freezing point is worked out for a determinate quantity of the substance dissolved in 100 grams of water, the result, which he terms the "*coefficient of depression*," is constant for the same substance, and that the coefficients for different substances bear a simple relation to their molecular weights. It was left for Raoult to show clearly what those relations are, and to extend the investigation to organic substances, and to other solvents besides water.

Briefly stated, Raoult's generalisations are as follow:—When certain quantities of the same substance are successively dissolved in a solvent on which it has no chemical action, there is a progressive lowering of the point of congelation of the solution, and this lowering is *proportional to the weight of the substance dissolved in a constant weight of the solvent;* in other words, the lowering of congelation is dependent solely on the respective masses of the substance and solvent, and is independent of the temperature.

If the observed depression of the point of congelation of a solution be taken as C, and the weight in grams of the anhydrous substance in 100 grams of the solvent as P, then, when the substance exists in solution in the anhydrous state, the quotient $\frac{C}{P}$, which we will represent by A, and which Raoult terms "gross coefficient of depression" (*coefficient d'abaissement brut*), is the lowering of congelation produced by 1 gram of substance in 100 grams of solvent. If we multiply this coefficient, $\frac{C}{P} = A$, by the molecular weight of the body dissolved, we obtain the depression which would be produced if 1 mol.* of the substance were dissolved in 100 grams of the solvent. This is the "true molecular depression" (*abaissement moléculaire vrai*) which is represented by T.

We have then—

$$T = \frac{C}{P} \times M.$$

This formula Raoult finds to be sensibly correct, even for substances which do not exist in solution in the anhydrous form, provided we take solutions so dilute that the observed lowering of congelation C is about 1° C.

* By "1 mol. of substance" dissolved in 100 grams of water, Raoult means of course a weight of the substance in grams equal to its molecular weight.

T is a quantity varying with the nature of the solvent, *but with the same solvent remaining constant for numerous groups of compounds*, and it may consequently be considered as a known quantity. On the other hand, the *coefficient* of depression $\frac{C}{P}$ or A can be obtained experimentally, so that if the molecular weight M of the substance is unknown, it can be calculated by the formula—

$$M = \frac{T}{A},$$

and from amongst the possible molecular weights of the substance under experiment, we take that which approaches nearest to $\frac{T}{A}$.

In carrying out this method, any liquid may be used as a solvent, provided it is capable of solidifying at a definite temperature. It suffices merely to know the value of T for that particular solvent, and for certain groups of bodies analogous to the one under experiment. The solvents which Raoult recommends in his latest paper (*Ann. Chim. Phys.* [6], **8**, 317, 1886) are water, acetic acid, and benzene.

For *inorganic salts*, the values of T for water have been found by Raoult to be six in number, corresponding to certain well-defined groups of salts: with benzene, the values of T are reduced to two, and for acetic acid T has a constant value for all inorganic compounds. With *organic* compounds, with but very few exceptions, the respective values of T for the solvents mentioned above remain constant; they are as follows:—

	T.
Water	19
Acetic acid	39
Benzene	49

Raoult has examined a large number of organic substances, the molecular weights of which have been put beyond doubt by determinations of their vapour-densities, and the results illustrate in a remarkable manner the accuracy and general application of his method. In determining the value of T for water, Raoult has recorded in his tables numbers which he obtained for cane-sugar, invert-sugar, milk-sugar, and mannitol, and which indicate that the commonly received formulæ for these substances express their molecular composition, but he does not call any special attention to these experiments, nor does he appear to have examined any other of the carbohydrates. It seemed therefore a matter of interest, in the present state of our knowledge of this important group of substances, to submit its various members to a method which promises, in the

near future, to throw much light on the molecular size of non-volatile organic compounds.

Owing to the comparative ease with which most of the carbohydrates, with the exception of dextrose and levulose, are hydrolised, the employment of acetic acid as a solvent was impracticable, and our choice was necessarily limited to that of water. With the exception of oxalic acid and the amines, all the bodies examined by Raoult in aqueous solution give normal results.

The method of experiment we have adopted is extremely simple, and is essentially the same as that described by Auwers (*Ber.*, 1888, 712), with the exception that when working with aqueous solutions, it is not necessary to take any precautions to exclude the air. A solution of the carbohydrate is prepared, containing a known weight of the substance in 100 c.c. of the liquid. About 120 c.c. of this are introduced into a thin beaker of about 400 c.c. capacity, closed with an india-rubber plug with three perforations, through one of which a small glass stirrer passes, and through the second a thermometer graduated to $\frac{1}{10}$th of a degree C. This is viewed through a telescope, and since the scale is an open one, there is no difficulty in taking readings to $\frac{1}{100}$th of a degree. The beaker is immersed in a mixture of ice and brine at a temperature from 2° to 3° below the freezing point of the solution, which is allowed to fall in temperature from 0·5° to 1° below its point of congelation; this it will readily do without the formation of ice. Freezing is now brought about by dropping into the beaker, through the third aperture in the plug, a very small fragment of ice from a little of the same solution which has been previously frozen in a test-tube. The liquid is stirred briskly, and as freezing commences the thermometer rises very rapidily, and, in a few seconds becomes stationary at the true freezing point of the solution, the concentration being always so arranged that the observed depression is never more than 1° to 2° below zero.

If we take

C = observed depression of freezing point,
x = grams of substance in 100 c.c. of solution,
y = grams of water in 100 c.c. of solution,

then the "coefficient of depression" is expressed by the equation

$$\frac{C \times y}{x \times 100} = \frac{C}{P} = A,$$

and the molecular weight M of the substance by

$$M = \frac{19}{A}.$$

As the molecular composition of dextrose may be looked upon as fairly well established, it will be well, in the first place, to show how far Raoult's method, when applied to this substance, bears out the generally accepted formula $C_6H_{12}O_6$.

In all the experiments which follow,

Column E gives the observed temperature.
" C " the depression of freezing point, *corrected*.*
" A " the "coefficient of depression."
" M " the molecular weight deduced from experiment.

Dextrose, $C_6H_{12}O_6$. M = 180.

Freezing point of water used 0°·000.

Strength of solution, 12·616 grams dextrose in 92·25 grams water.

E.	C.	A.	M.
−1·450°	1·450°	0·106	179
−1·450	1·450	0·106	179
−1·450	1·450	0·106	179

Strength of solution, 8·3704 grams dextrose in 94·86 grams water.

E.	C.	A.	M.
−0·945°	0·945°	0·107	177
−0·940	0·940	0·106	179
−0·940	0·940	0·106	179

Strength of solution, 4·1140 grams dextrose in 97·47 grams water.

E.	C.	A.	M.
−0·445°	0·445°	0·103	184
−0·445	0·445	0·103	184
−0·440	0·440	0·104	182

Calculated for $C_6H_{12}O_6$.	Found (Mean).
A = 0·106	A = 0·1052
M = 180·0	M = 180·2

These experiments with dextrose show very clearly the concordant nature of the results obtained by this method, even when the solutions vary considerably in density.

If dextrose had been a previously unknown substance, whose relations and derivatives had not been studied, and for which only

* The correction here applied is the difference between the observed freezing point of the solution and the freezing point of water determined in the same apparatus, and under exactly similar conditions.

the empirical formula CH_2O had been determined by combustion, we should have had no hesitation in selecting from among the possible molecular weights, 30, 60, 90, 120, 150, 180, 210, &c., the one which corresponds most nearly with the observed value of M = 180, and with the formula $C_6H_{12}O_6$.

Dextrose exhibits in a pre-eminent degree the phenomenon of *birotation;* the action on polarised light of a freshly-prepared solution of crystallised dextrose being double that of the same solution after standing for some hours. The phenomenon of birotation has never received any physical explanation, and as it seemed to us possible that it might be in some way intimately connected with the size of the molecule in solution, we submitted to Raoult's method freshly prepared solutions in which the amount of birotary carbohydrate was concurrently estimated by the polariscope.

Freezing point of water used, +0·025°.

Strength of solution, 10·013 grams dextrose in 93·85 grams water.

E.	C.	A.	M.
−1·115°	1·140°	0·106	180

$[\alpha]_j$ at time of experiment 105·6° = 72·6 *per cent. birotary dextrose.*

E.	C.	A.	M.
−1·115°	1·140°	0·106	180

$[\alpha]_j$ at time of second experiment 97·2° = 58·6 *per cent. birotary dextrose.*

Calculated for $C_6H_{12}O_6$.	Found.
A = 0·106	A = 0·106
M = 180·0	M = 180·0

It is clear from the above, that whatever may be the cause of birotation it is certainly not to be attributed to a condensation of the molecule.

Cane-sugar. $C_{12}H_{22}O_{11}$. M = 342.

Freezing point of water used, 0·000.

Strength of solution, 13·052 grams in 91·98 grams water.

E.	C.	A.	M.
−0·825°	0·825°	0·059	322
−0·835	0·835	0·058	328
−0·835	0·835	0·058	328

Strength of solution, 10·1410 grams sugar in 93·77 grams water.

E.	C.	A.	M.
−0·600°	0·600°	0·055	345
−0·600	0·600	0·055	345
−0·600	0·600	0·055	345

Strength of solution, 8·2580 grams sugar in 94·93 grams water.

E.	C.	A.	M.
−0·500°	0·500°	0·057	333
−0·490	0·490	0·056	340
−0·490	0·490	0·056	340

Strength of solution, 6·064 grams sugar in 96·28 grams water.

E.	C.	A.	M.
−0·355°	0·355°	0·056	340
−0·355	0·355	0·056	340
−0·350	0·350	0·055	345

Calculated for $C_{12}H_{22}O_{11}$.	Found.
A = 0·0555	A = 0·0562
M = 342·0	M = 337·5

The lowest possible empirical formula, $C_{12}H_{22}O_{11}$, evidently represents the molecule of cane-sugar in solution, and our results consequently do not bear out a suggestion which Winter appears to make in his recent paper on levulose (*Annalen*, **244**, 1888, 308) that the molecule of cane-sugar is more complex than this.

Inverted Cane-sugar.

Since the molecular weight of cane-sugar is 342, and that of dextrose 180, it seemed almost certain that Raoult's method applied to invert-sugar would yield a value for M of 180, and that the value of A would consequently be approximately doubled during the process of inversion.

The experiment was made by determining the depression of the freezing point of the *same solution* of cane-sugar, both before and after inversion, which was brought about by the addition of a little *invertase*.*

* Invertase is readily prepared by triturating fresh solid yeast with fine sand, digesting the pasty mass with water at the ordinary temperature for a few hours, filtering, and precipitating the filtrate with alcohol of about 80 per cent. The precipitate is well washed with alcohol, dehydrated with absolute alcohol, and dried over sulphuric acid in a vacuum. As thus prepared, *invertase* is a white, friable substance, completely soluble in water, and readily inverting several hundred times its own weight of cane-sugar.

The results were as follows :—

Cane-sugar Solution before Inversion.

Freezing point of water, +0·025°.
Strength of solution, 4·9818 grams sugar in 96·94 grams water.

E.	C.	A.	M.
−0·270°	0·295°	0·058	328
−0·270	0·295	0·058	328
−0·275	0·300	0·058	328

Calculated for $C_{12}H_{22}O_{11}$.	Found (mean).
A = 0·0555	A = 0·058
M = 342·0	M = 328·0

The above solution was completely inverted with 0·030 gram of invertase, the volume being maintained constant; it gave

After Inversion.

Freezing point of water +0·025°.
Strength of solution, 5·344 grams sugars in 96·72 grams water.

E.	C.	A.	M.
−0·585°	0·610°	0·110	173
−0·580	0·605	0·109	175
−0·580	0·605	0·109	175

Calculated for $C_6H_{12}O_6$.	Found (mean).
A = 0·106	A = 0·1093
M = 180·0	M = 174·3

This experiment may be taken as a proof that the value of M for levulose, like that for dextrose, is 180.

Maltose. $C_{12}H_{22}O_{11}$. M = 342.

That this is a saccharose having the same elementary percentage composition as cane-sugar there can be but little doubt, but whether these two compounds are metameric or polymeric is still open to question. The metallic derivatives and acetyl compounds of maltose tend to show that the simplest possible formula, $C_{12}H_{22}O_{11}$, also expresses its molecular composition, but Herzfeld has recently questioned this (*Annalen*, **220**, 1883, 220) and is inclined, from his

experiments on the behaviour of maltose towards Fehling's solution, to assign to it a molecular formula at least three times as large. To put this matter to the test of direct experiment, the following determinations were made by Raoult's method:—

Freezing point of water, +0·030.

Strength of solution, 15·785 grams maltose in 90·40 grams water.

E.	C.	A.	M.
−1·010°	1·040°	0·059	322
−1·000	1·030	0·059	322
−1·005	1·035	0·059	322

Strength of solution, 10·499 grams maltose in 93·68 grams water.

E.	C.	A.	M.
−0·635°	0·665°	0·059	322
−0·635	0·665	0·059	322
−0·635	0·665	0·059	322

Strength of solution, 5·124 grams maltose in 96·89 grams water.

E.	C.	A.	M.
−0·285°	0·315°	0·059	322
−0·285	0·315	0·059	322
−0·285	0·315	0·059	322

Calculated for $C_{12}H_{22}O_{11}$.	Found (mean).
A = 0·0555	A = 0·059
M = 342·0	M = 322·0

These experiments prove beyond doubt that the molecules of cane-sugar and maltose, when in solution, are of equal size, and that these substances are therefore metameric, not polymeric. We must consequently attribute the difference in their properties to the different arrangement of atoms in the molecule.

Milk-sugar, $C_{12}H_{22}O_{11}$. M = 342.

Freezing point of water, +0·030°.

Strength of solution, 10·263 grams in 93·59 grams water.

E.	C.	A.	M.
−0·580°	0·610°	0·055	345
−0·585	0·615	0·055	345
−0·585	0·615	0·055	345

Calculated for $C_{12}H_{22}O_{11}$.	Found.
A = 0·0555	A = 0·055
M = 342·0	M = 345·0

These results indicate that the usually accepted formula for milk-sugar expresses its molecular composition, and that the suggestion made by Herzfeld (*Annalen*, **220**, 1883, 222) that the true formula is a multiple of $C_{12}H_{22}O_{11}$, is not correct, but that the three sugars of the saccharose group, cane-sugar, maltose, and milk-sugar, have the same molecular weight.

Arabinose, $C_5H_{10}O_5$. M = 150.

This sugar, a product of the action of dilute acid on gum-arabic, was formerly considered to have the formula $C_6H_{12}O_6$. Recent researches of Kiliani (*Ber.*, **20**, 1887, 343 and 2710) have, however, established the fact that it is a compound with only 5 atoms of carbon, and that it is represented by the formula $C_5H_{10}O_5$.

We have submitted this substance to Raoult's method, with the following results, having first convinced ourselves of its purity by a determination of its optical activity :—

Freezing point of water, +0·030°.

Strength of solution, 4·1355 grams in 97·45 grams water.

E.	C.	A.	M.
−0·510°	0·540°	0·127	149·6
−0·505	0·535	0·126	150·7
−0·505	0·535	0·126	150·7

Calculated for $C_5H_{10}O_5$.	Found (mean).
A = 0·126	A = 0·1263
M = 150·0	M = 150·3

These results fully confirm Kiliani's conclusions.

Raffinose.

This sugar, which occurs in the molasses of beet-sugar, and in the seeds of various plants, has been the subject of considerable investigation. It crystallises in well-defined needles or prisms, and from analyses the formula $C_{18}H_{32}O_{16},5H_2O$, or a multiple of this, has been deduced, preference being given to a molecule represented by double this formula.

We are indebted to Dr. Griess for a specimen of pure crystalline raffinose, as well as that of the pure arabinose mentioned above.

The substance had an optical activity of $[\alpha]_j$ 116·6°, or $[\alpha]_D$ 104·6, which agrees exactly with the numbers given by Tollens for hydrated raffinose.

Freezing point of water, +0·030°.

Strength of solution, 8·2225 grams hydrated substance in 94·51 grams water.

E.	C.	A.	M.
−0·280°	0·310°	0·0356	533
−0·280	0·310	0·0356	533
−0·290	0·320	0·0367	518

Calculated for $C_{18}H_{32}O_{16},5H_2O$.	Found (mean).
A = 0·032	A = 0·036
M = 594·0	M = 528·0

Our results indicate that the molecule of raffinose approximates to the above formula, and that it is not a multiple of this.

Mannitol, $C_6H_{14}O_6$. M = 182.

Although this substance is not strictly included in the ordinarily accepted definition of a carbohydrate, yet its relations to the group are of so intimate a nature, and the size and constitution of its molecule have been so accurately determined by its reactions, that we have considered it well, as a further proof of the accuracy of Raoult's method when applied to compounds of this class, to include the results of its examination.

Freezing point of water, +0·030°.

Strength of solution, 7·5382 grams in 95·09 grams water.

E.	C.	A.	M.
−0·805°	0·835°	0·105	181
−0·805	0·835	0·105	181
−0·805	0·835	0·105	181

Calculated for $C_6H_{14}O_6$.	Found.
A = 0·104	A = 0·105
M = 182·0	M = 181·0

The application of this new method to starch, and to the non-crystallisable products of its transformation, soluble starch, the dextrins and malto-dextrin, seemed full of promise, since chemists are still divided in their opinions as to the true nature of these compounds, and as to whether the differences in the properties of the dextrins are such as to justify the view that they are polymeric, or, on the other hand, compounds having the same molecular weight, but differing in constitution.

Certain difficulties have, however, arisen at this stage of our inquiry, owing to the very high molecular weight which these substances evidently possess. As a result of this, the freezing point of even very strong solutions is depressed to such a small extent as to render it necessary, before we can assign any approximately accurate numerical value to our results, to determine the limits of error of the method, which manifestly increase with the molecular weight of the substance. We have, however, convinced ourselves that the molecular complexity of these compounds is very great indeed, and we hope to lay certain results before the Society at an early date.

XLVI.—*The Molecular Weights of Nitrogen Trioxide and Nitric Peroxide.*

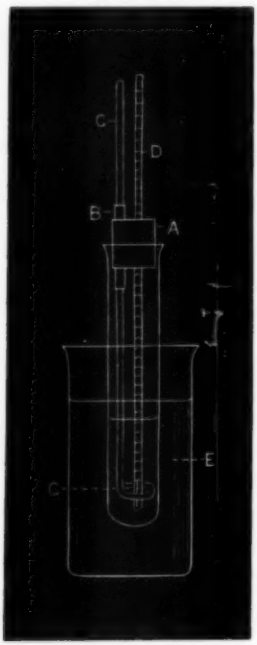
By W. Ramsay, Ph.D.

It was shown by Dr. Sydney Young and myself in a paper read before the Physical Society (*Proc. Phys. Soc. Lond.*, 1887, **9**, 45), that the Messrs. Natanson's experiments on the relations between the pressure, temperature, and volume of nitric peroxide, interpreted by the light of the equation $p = bt - a$ (see previous communications to the Physical Society), lead to the probable conclusion that at low temperatures the formula of the peroxide is N_2O_4, and that no more complex molecular groupings are formed than those corresponding to $2NO_2$. But owing to experimental difficulties, it appears to be impossible to prove this statement with absolute certainty from experiments on the density of the substance in the gaseous state.

A means of determining the molecular weight of liquid and solid substances has, however, recently been placed at the disposal of chemists by the brilliant researches of M. Raoult. In a series of memoirs published in the *Annales de Chimie et de Physique* [5], **20**, 217; **28**, 133; [6], **2**, 66, 93, 99, 115; **4**, 401; **8**, 289, 317) he has proved that the depression of the freezing point of a liquid caused by the presence of dissolved liquid or solid is proportional to the absolute amount of substance dissolved, and inversely proportional to its molecular weight. This law holds for the great majority of substances with which he has experimented, and the exceptions are so few in number, and so striking, as to call for further research to explain their anomalous behaviour. With glacial acetic acid as solvent, however, among nearly 150 substances with which he experimented, there are barely half-a-dozen whose behaviour proved abnormal.

This method makes it possible to determine the molecular weight of liquid nitric peroxide; and it also throws light on the question whether nitric peroxide undergoes further dissociation at low temperatures by dilution, which may be regarded as equivalent to reduction of pressure, if the liquid and gaseous states be compared with one another.

Experiments (an account of which follows) tend to show that not merely is the formula of nitric peroxide N_2O_4 at temperatures in the neighbourhood of 16°, but also that no appreciable alteration in molecular weight is produced by considerably increasing the relative number of molecules of the peroxide in a given volume.



The accompanying diagram shows a convenient form of the apparatus required for such experiments. A wide test-tube is closed by an india-rubber cork A, perforated with two holes. Through one of these a piece of wide glass tubing B passes, in which a stirrer CC moves freely up and down. The thermometer D serves to show the temperature of the liquid, while by surrounding the tube by a beaker E with hot or cold water as required, the temperature may be raised a few degrees above, or depressed a few degrees below the freezing point of the solvent.

A quantity of acetic acid, fractionated from water, amounting to 41·02 grams, was weighed out. It melted at 16·680°. A small bulb containing 0·378 gram of nitric peroxide was added and broken in the acetic acid by crushing it with the stirrer. The melting point of the acid was lowered by this addition to 16·300°. The depression is therefore 0·380°. Had one part of peroxide been added to 100 parts of acetic acid, the depression would have been, according to this measurement, 0·4214°. And 0·4214 × 94·6 = 39 (Raoult's constant for acetic acid); hence the molecular weight of the peroxide appears from this experiment to be 94·6. Without disturbing the apparatus, a second bulb of peroxide weighing 0·5085 gram was crushed in the acid, and the melting point was now 15·825°; the total depression amounting to 0·855°. Calculating as before, the depression for 1 gram per 100 is 0·3956, and the molecular weight 98·58. Subsequent additions were made as follows:—

1·5405	gram	lowered the melting point	1·590°	; mol. wt.	= 92·11.
2·2080	,,	,, ,,	2·280	,,	= 92·07.
3·1510	,,	,, ,,	3·215	,,	= 93·18.
3·679	,,	,, ,,	3·865	,,	= 90·29.

A second determination gave the following result:—

Acetic acid taken, 40·05 grams, melting at 16·675°; the addition of 0·893 gram of the peroxide lowered the melting point to 15·768°; depression = 0·907°. Depression produced by 1 gram per 100 would therefore amount to 0·4068°; and the molecular weight is therefore 95·87.

It must therefore be concluded that the molecular weight of nitric peroxide in the liquid state at about 16° is 92, and its formula consequently is N_2O_4. It is also manifest that the relative number of molecules of the peroxide in a given volume of acetic acid may be decreased from 8·97 to 0·92 without materially altering the molecular weight; no dissociation, therefore, would appear to take place on dilution.

Similar experiments were tried with nitrogen trioxide prepared by dissolving N_2O_4 in acetic acid and passing NO through the cooled mixture; but they gave no reliable results owing to the dissociation of the trioxide, which is rapid at 16°.

XLVII.—*The Action of Heat on the Salts of Tetramethylammonium.*

By A. T. Lawson and Norman Collie, PhD., F.R.S.E.

The following experiments on the action of heat on the tetramethylammonium salts were undertaken in order to ascertain in what respects the compound ammonium salts when subjected to the action of heat resembled, and also in what points they differed from, the corresponding phosphorus and sulphur salts.

The action of heat on a considerable number of the trimethylsulphine salts (chiefly the salts of sulphur acids) has been investigated by Crum-Brown and Blaikie (*J. pr. Chem.* [2], **23**, 395); whilst the action of heat on the tetramethylphosphonium salts is the subject of a separate paper by one of us (p. 636), but the decomposition that the tetramethylammonium salts suffer when heated has only been studied in a very few cases. Hofmann (*Ber.*, **14**, 494) has noticed that the hydroxide is easily decomposed by heat—

$$(CH_3)_4N{\cdot}OH = (CH_3)_3N + CH_3{\cdot}OH,$$

whilst Thompson (*Ber.*, **16**, 2339) has found that the cyanide volatilises unchanged.

The salts that tetramethylammonium hydroxides form with the more common acids have not received much attention since Hofmann discovered these interesting compounds nearly 40 years ago. Duvillier and Buisine (*Ann. Chim. Phys.* [5], **23**, 331) have shown that methyl nitrate, and also methyl bromide, when heated with methylamine or with dimethylamine, yield tetramethylammonium compounds, but they did not prepare many of the salts. Hofmann mentions that crystalline salts can be prepared by neutralising the base with sulphuric, oxalic, or nitric acids, and he also prepared the chloride, but he gives no details as to the solubility, crystalline form, or other properties of these compounds. The bromide and cyanide have been prepared by other workers, and also a number of double salts; but the chief work on the tetramethylammonium compounds seems to have been directed towards the preparation of a number of addition products, obtained by the action of chlorine, bromine, or iodine on the halogen salts (Waltzien, *Annalen*, **99**, 1; Stahlschmidt, *Jahresber.*, 1863, 403; Dobbin, *J. Chem. Soc.*, Trans., 1886, 846).

The starting point from which we prepared all our salts was the iodide of tetramethylammonium. It was made according to the method suggested by Hofmann. Methyl alcohol saturated with ammonia gas was digested with methyl iodide in sealed tubes at a temperature of 100—120°. It was found better to put the methyl

iodide in a separate tube (open at one end), and not to mix it with the ammoniacal methyl alcohol till after the tube which contained both had been sealed. The yield varied considerably in different tubes, several tubes, after heating for only a few hours, being filled with crystals, while the yield in other tubes, even on prolonged heating at a temperature of 140°, did not seem to be materially increased. We believe this was due possibly to the presence of small quantities of water in the methyl alcohol. The iodide of tetramethylammonium can be easily separated from the iodide of ammonium, and from the hydriodides of mono-, di-, and tri-methylamine by crystallisation from water, in which it is not very soluble. The mean of several analyses of the salt gave 63·1 per cent. of iodine, the theoretical amount required by $(CH_3)_4NI$ being 63·2 per cent. iodine.

When this salt is heated, it decomposes at a temperature not much short of a low red heat without melting, giving trimethylamine, free iodine, and other products. It probably first splits up into trimethylamine, and iodide of methyl—

$$(CH_3)_4NI = (CH_3)_3N + CH_3I,$$

and at the high temperature both the trimethylamine and the iodide of methyl are partially decomposed (the latter almost completely).

Action of Heat on Bromide of Tetramethylammonium.

This salt was prepared by neutralising hydroxide of tetramethylammonium with hydrobromic acid, and evaporating the solution over the water-bath. On allowing the salt to remain over sulphuric acid in a vacuum, it soon crystallised. An analysis of the salt gave the following results: 0·430 salt took 27·7 c.c. decinormal $AgNO_3$ solution = 51·5 per cent. bromine; theory for $(CH_3)_4NBr$ = 51·9 per cent. bromine. It forms needle-shaped crystals which are deliquescent, and their solubility in water is considerably greater than that of the iodide; 100 c.c. of water at 15° dissolve 55·26 grams of the salt.

The salt on heating to 300° in a vacuum gave off no gas, but on raising the temperature above 360° the salt sublimed and condensed again on the walls of the tube (which was used as a condenser and was surrounded by a freezing mixture) in the form of a white powder. This solid was analysed, and from a bromine determination proved to be pure bromide of tetramethylammonium. (It contained 51·6 per cent. bromine.) At the end of the experiment, the whole of the salt had sublimed, and scarcely a trace of permanent gas had been evolved. Evidently the bromide on heating dissociates—

$$(CH_3)_4NBr = (CH_3)_3N + CH_3Br,$$

and the two gases at once recombine on cooling.

Action of Heat on Chloride of Tetramethylammonium.

The chloride was prepared by treating the iodide with hydroxide of silver, and neutralising the base thus obtained with hydrochloric acid. The solution was evaporated over the water-bath to the consistency of a syrup, and allowed to stand in a vacuum over sulphuric acid, when it soon crystallised. Attempts made to determine its solubility in water were unsuccessful, on account of its great solubility; it is also deliquescent. The salt was heated in a vacuum at 150° till perfectly dry, when a chlorine determination gave 32·4 per cent. of chlorine: $(CH_3)_4NCl$ contains 32·4 per cent. Cl.

When the salt is heated to above 360°, it decomposes completely without the slightest charring, yielding trimethylamine and a gas which burnt with a greenish flame, and behaved in every way like chloride of methyl. In one experiment, 3·52 grams of salt yielded 750 c.c. of gas. The theoretical yield of methyl chloride would be about 800 c.c. The trimethylamine was converted into the chloroplatinate, and gave the following numbers on analysis.

0·144 gram salt gave 0·0527 gram Pt = 36·60 per cent. Pt. Theory for $(Me_3HNCl)_2PtCl_4$ = 36·93 per cent. Pt.

The gas was also analysed:—

Gas taken	8·0 c.c.
Gas and oxygen	31·0 „
After explosion and the addition of a few drops of water	19·8 „
After addition of caustic soda	12·0 „

This shows that one volume of the gas on explosion with excess of oxygen yields nearly its own volume of carbon dioxide, which is the amount required by methyl chloride. The decomposition of the chloride is nearly quantitative, and can be expressed by the following equation:—

$$(CH_3)_4NCl = (CH_3)_3N + CH_3Cl.$$

Action of Heat on Fluoride of Tetramethylammonium.

After the extremely neat manner in which the chloride decomposed when heated, we had every reason to expect that the fluoride would decompose in an analogous manner, yielding trimethylamine and methyl fluoride, and the decomposition, besides being of interest in illustrating the general method of decomposition of the tetramethylammonium salts, would also be useful in the preparation of organic fluorine compounds.

Although fluorine itself has recently been isolated, still, on account of the great difficulty of uniting fluorine with carbon, the number of organic compounds where fluorine is combined with hydrocarbon radicles of the paraffin series is small, and their properties have not been much studied.

The salt was prepared in a manner similar to that employed in the manufacture of the chloride. The base was neutralised with hydrofluoric acid, and evaporated over the water-bath to a syrup. This solidified on cooling to a solid mass of radiating crystals. They were, however, by no means dry, for on heating at 100° in a vacuum, a considerable amount of water was lost. Great difficulty was experienced in drying the salt completely, and it could only be accomplished by prolonged heating in a vacuum at 160°. A determination was made of the amount of water contained in the salt which had been dried over sulphuric acid.

0·900 gram salt heated at 160° in a vacuum lost 0·150 gram H_2O = 16·6 per cent. H_2O.

	Theory for Me_4NF,H_2O.	Found.
H_2O.....	16·2 per cent.	16·6 per cent.

The tube in which the salt was heated was not etched, showing that no hydrofluoric acid had been liberated. Some of the dried salt was analysed :—

I. 0·500 gram salt gave 0·1975 gram CaF_2 = 19·2 per cent. fluorine.

II. 0·2727 gram salt gave 0·1186 gram CaF_2 = 21·1 per cent. fluorine.

	Calculated for Me_4NF.	Found. I.	Found. II.
F.....	20·4 per cent.	19·2	21·1 per cent.

The great difference in the percentage of fluorine found is possibly due to the great difficulty in obtaining the salt pure and dry at the same time, for if the salt be heated even as high as 160° in a vacuum it is not perfectly anhydrous, and if the temperature be raised above that point it begins to slowly decompose.

When the salt is heated to 180° in a vacuum it begins to decompose, and yields trimethylamine and a gaseous substance. During the first experiments made on the action of heat on this salt, the trimethylamine was condensed by passing the products of the decomposition through a U-tube surrounded by a freezing mixture. Subsequently it was found better to absorb the trimethylamine by pumice-

stone moistened with sulphuric acid (which absorbed only the trimethylamine). The trimethylamine obtained was converted into the chloroplatinate, and analysed (0·362 gram salt gave 0·132 gram Pt = 36·6 per cent.; theory for $(Me_3HNCl)_2PtCl_4$ = 36·9 per cent. Pt).

The amount of tetramethylammonium fluoride which was decomposed was also noticed, as well as the amount of gas evolved. 2·614 grams of the fluoride gave 400 c.c. of gas, which proved to be fluoride of methyl. This gas was first prepared by Dumas and Peligot (*Annalen*, **15**, 59), by heating together potassium fluoride and potassium methyl sulphate. The gas prepared by heating the fluoride of tetramethylammonium was slightly soluble in water, but more so in alcohol; it burnt with a blue flame, yielding hydrofluoric acid, and it had a pleasant odour. On analysis, it yielded its own volume of carbon dioxide:—

Taken of gas.....	8·0 c.c.
Gas and oxygen	51·0 „
After explosion.....	39·0 „
After addition of caustic soda.	31·0 „

thus showing that 8·0 c.c. of gas yielded 8·0 c.c. of carbon dioxide. The fluoride of tetramethylammonium, therefore, decomposes in a manner similar to the chloride:—

$$(CH_3)_4NF = (CH_3)_3N + CH_3F.$$

Action of Heat on Nitrate of Tetramethylammonium.

The salt was prepared by the action of silver nitrate on the iodide. Evaporated over the water-bath to a small bulk, the solution crystallises in long needles; when pure, it does not seem to be perceptibly deliquescent. Several grams of the salt were heated. No decomposition occurred till the temperature had risen to above 300°. Slight blackening then took place, but it was found that if the temperature was kept just at the melting point of the salt, nearly the whole of it decomposed without much charring. A yellow liquid was found in the condensing apparatus, and a small quantity of gas was produced, consisting chiefly of nitric oxide, but on treatment with oxygen and water there remained a small amount, which from its properties seemed to be methyl nitrate; the quantity, however, was too small for identification. The yellow distillate was alkaline, and smelt strongly of trimethylamine, it was, therefore, warmed with water, in order to free it from the base, and then treated with a small quantity of pure caustic soda; on warming, a further quantity of trimethylamine

was evolved, which gave the characteristic chloroplatinate. The remaining caustic soda solution was treated with carbon dioxide, and evaporated to dryness, it was then extracted with absolute alcohol, and the alcoholic solution of the sodium salt evaporated to dryness. Thus treated a small quantity of a soluble sodium salt was obtained. An attempt to prepare the silver salt was unsuccessful, owing to the reduction of the salt to metallic silver; with mercurous salts a similar reduction took place, and the sodium salt itself gave carbon monoxide when heated with strong sulphuric acid; the salt in question was, therefore, probably sodium formate. From this it will be seen that the decomposition of the nitrate is complex, trimethylamine alone being formed in any quantity. If methyl nitrate is also formed, it is decomposed, yielding as oxidation products, formic acid, &c., and as reduction products, methyl nitrite and nitric oxide.

Action of Heat on Nitrite of Tetramethylammonium.

This salt was prepared by treating a solution of iodide of tetramethylammonium with nitrite of silver. It is deliquescent, and much more soluble in water than the nitrate. When subjected to the action of heat, it decomposed at a temperature above 300° with great rapidity; trimethylamine was produced, and at the same time a small quantity of an orange-coloured oxide of nitrogen mixed with a considerable amount of some other gas was given off. On treatment with caustic soda, there was little diminution in volume, but on adding oxygen the orange peroxide of nitrogen was produced, which dissolved in the caustic soda solution. About half of the gas collected consisted of nitric oxide, and the remainder was inflammable. This residual gas was mixed with an equal volume of oxygen (under the supposition that it was methyl nitrite), and exploded in a eudiometer. The result was unexpected, for the two volumes of mixed gases became nearly five volumes, and the remaining gas was inflammable; evidently the oxygen used was not nearly sufficient for its combustion, and another experiment was, therefore, made with the following quantities:—

Gas used	5·0 c.c.
Gas and oxygen	37·0 „
After explosion.....	24·0 „
After treatment with caustic soda	14·4 „

Thus 5·0 c.c. of the gas yielded 9·6 c.c. of carbon dioxide, or nearly twice the volume, and the remaining gas in the eudiometer was nearly pure oxygen. This proved that the gas under examination

did not contain nitrogen, and also that two atoms of carbon were present in the molecule; in all probability the substance was methyl ether. For when mixed with its own volume of oxygen, and exploded, two volumes would give five volumes of mixed and inflammable gases:—

$$\underbrace{C_2H_6O + O_2}_{\text{2 vols.}} = \underbrace{CO_2 + CO + 3H_2}_{\text{5 vols.}}$$

whilst if it were exploded with excess of oxygen it should yield twice its volume of carbon dioxide:—

$$2C_2H_6O + 6O_2 = 4CO_2 + 6H_2O.$$

Evidently, then, when the nitrite is heated, it is decomposed into trimethylamine and nitrite of methyl, the latter being further decomposed into methyl alcohol, nitric oxide, and oxygen:—

$$(CH_3)_4N\cdot NO_2 = (CH_3)_3N + CH_3NO_2.$$
$$4CH_3NO_2 = 2(CH_3)_2O + 4NO + O_2.$$

The nitric oxide and oxygen on cooling combined, forming some of the higher oxides of nitrogen, which probably united with the trimethylamine.

Action of Heat on Acetate of Tetramethylammonium.

The hydroxide of tetramethylammonium was neutralised with acetic acid in order to produce this salt; the solution was evaporated, and solidified to a mass of needle-shaped crystals when allowed to stand in a vacuum over sulphuric acid. The salt was highly deliquescent. When heated, it melted at about 70°, and a small quantity of water distilled; at 190—200°, complete decomposition took place. The condenser, which was surrounded by a freezing mixture, contained a liquid, which on the addition of water separated into two layers, one of which proved to be an aqueous solution of trimethylamine, whilst the other was acetate of methyl. This was proved beyond doubt by the boiling point, 57—58° (methyl acetate, b. p. 56°), and by its conversion into methyl alcohol and sodium acetate on treatment with caustic soda. The sodium acetate was converted into the corresponding silver salt, and then analysed. 0·5395 gram salt gave 0·348 Ag = 64·5 per cent.; theory for $AgC_2H_3O_2$ = 64·6 per cent. Ag. Some of the liquid b. p. 57·8°, was shaken with a concentrated solution of acid sulphite of sodium, but no crystalline double salt was formed. The decomposition of the acetate is, therefore, quite simple:—

$$(CH_3)_4N\cdot C_2H_3O_2 = (CH_3)_3N + CH_3\cdot C_2H_3O_2.$$

Action of Heat on Benzoate of Tetramethylammonium.

This salt was prepared in the same way as the acetate. It is a deliquescent salt, but could be obtained in the form of long needles by allowing the salt to remain over sulphuric acid in a vacuum. When it was heated, it melted at 220—230°, and at once decomposed. There was no charring, and the whole of the salt distilled by the time the temperature had risen to 250°. No gas was produced by the action of heat. The distillate was completely liquid, and separated into two layers when water was added, the one an aqueous solution of trimethylamine, the other a liquid which when dried over calcium chloride and distilled, boiled at 198° (methyl benzoate, b. p. 199°). It did not contain nitrogen, and in order to be sure that it was methyl benzoate it was boiled with caustic soda. The distillate contained methyl alcohol, and from the residue containing the sodium benzoate, the silver salt was prepared. 0·230 gram salt gave 0·110 gram Ag = 47·1 per cent. Ag; theory for $AgC_7H_5O_2$ = 47·1 per cent. Ag. An analysis was also made of the chloroplatinate of trimethylamine. 36·5 per cent. Pt was found, while the theory for $(Me_3HNCl)_2PtCl_4$ = 36·7 per cent. Pt. The benzoate decomposes in exactly similar manner to the acetate:—

$$(CH_3)_4N\cdot C_7H_5O_2 = (CH_3)_3N + CH_3\cdot C_7H_5O_2.$$

Action of Heat on Sulphate of Tetramethylammonium.

This salt was obtained by neutralising the base with sulphuric acid. It is crystalline and very deliquescent, and, before the last traces of water could be removed, it had to be heated to about 160° in a vacuum. An analysis of some of the salt thus dried gave the following numbers:—

0·4342 gram salt gave $BaSO_4$ 0·417 gram = 39·57 per cent. SO_4.
Theory for $(Me_4N)_2SO_4$..... = 39·34 „ „

The remainder of the salt was carefully heated (5·72 grams). It melted at 280°, and at once began to decompose. The temperature was kept as near as possible to 290°, till all effervescence had ceased and the loss that the 5·72 grams had suffered was 1·42 grams. The whole of this was found to be due to the trimethylamine, no other substance passing over into the condenser. The salt on cooling solidified to a mass of deliquescent crystals which were broken up and analysed. They were found to contain sulphur, but their solution in water was not precipitated by a barium salt. The sulphur, therefore, had to be determined by a combustion of the substance (which Dr. Plimpton

kindly undertook, using his new method for analysing such compounds).

0·196 gram salt gave 0·2517 gram $BaSO_4$ = 17·63 per cent. S.

A determination of carbon and hydrogen was also made.

0·497 gram salt gave 0·590 CO_2 and 0·3765 H_2O = 32·38 per cent. C and 8·41 per cent. H.

	Calculated for $(CH_3)_4N\cdot(CH_3)SO_4$.	Found. I.	Found. II.
C.....	32·47	—	32·38
H	8·11	—	8·41
S.....	17·29	17·63	—
N.....	7·56	—	—
O.....	34·60	—	—

The first decomposition which the sulphate of tetramethylammonium suffers is the loss of trimethylamine, whereby it is converted into the methyl sulphate of tetramethylammonium.

$$(Me_4N)_2SO_4 = (Me_4)N\cdot MeSO_4 + Me_3N.$$

The 5·72 grams which were used should lose on heating 1·38 grams of trimethylamine, and the amount found was 1·42 gram. The further action of heat on the methyl sulphate of tetramethylammonium was complex; under these circumstances part of the salt passed over into the condenser unchanged, while compounds possessing a very strong smell, recalling that of sulphide of methyl, were formed. There was also produced in small quantities a highly crystalline substance which resembled dimethylsulphone, and much charred matter remained behind in the distilling flask.

Action of Heat on Oxalate of Tetramethylammonium.

Two methods were employed for the preparation of this salt—one by the action of oxalic acid on the base, the other by the action of silver oxalate on the iodide. A deliquescent salt was obtained by both methods, and was most difficult to obtain anhydrous. When allowed to remain in a vacuum over sulphuric acid, a crust formed on the surface of the salt, while the underlayer remained in a liquid state for weeks. The only method which gave at all a dry product was heating the salt in a vacuum at 160°. An analysis of some of the dry salt was made.

0·590 gram salt gave 0·1355 CaO = 36·35 per cent. C_2O_4.

Theory for $(Me_4N)_2C_2O_4$..... = 37·28 „ „

The rest of the salt was subjected to the action of heat. Scarcely any decomposition occurred below 360°, whilst above that temperature

the salt seemed to slowly sublime without melting; decomposition occurred at the same time, for trimethylamine and a gas were evolved. When the salt was more strongly heated, however, the evolution of gas became more rapid. The gas seemed to be composed of carbon dioxide mixed with nearly its own volume of carbon monoxide; a small quantity of an inflammable gas was also present. In two experiments made with weighed quantities of the oxalate, the following amounts of gas were obtained:—

I. 2·5 grams salt gave 500 c.c. of gas composed of 225 c.c. of carbon dioxide, 225 c.c. of carbon monoxide, and 50 c.c. of inflammable gas.

II. 2·4 grams salt gave 450 c.c. gas composed of 205 c.c. carbon dioxide and 205 c.c. of carbon monoxide and 40 c.c. of inflammable gas.

As far as could be ascertained, no methyl oxalate was formed; this was obviously due to the extremely high temperature at which the oxalate decomposed. Trimethylamine was formed in considerable quantity and was converted into the chloroplatinate and analysed. The decomposition of this salt is therefore not a simple one, owing to the high temperature at which it occurs. Probably methyl oxalate and trimethylamine are first formed, and the former at once decomposes into carbon dioxide, carbon monoxide, and other substances, perhaps methyl ether.

$$(Me_4N)_2C_2O_4 = 2Me_3N + Me_2C_2O_4,$$
$$Me_2C_2O_4 = Me_2O + CO + CO_2.$$

The amount of carbon dioxide and carbon monoxide evolved by the 2·4 grams and 2·5 grams respectively agrees fairly well with the amount required by theory; 2·4 grams should yield about 230 c.c., whilst 2·5 grams should yield about 245 c.c. of mixed gases.

Action of Heat on the Acid Carbonate of Tetramethylammonium.

A solution of the base saturated with carbon dioxide was evaporated, first over the water-bath and finally over sulphuric acid in a vacuum. The salt was crystalline but highly deliquescent, and could only be obtained anhydrous by prolonged heating in a vacuum. When subjected to the action of heat it began to decompose at 180° with effervescence, but more rapidly at a temperature of 210—220°. Trimethylamine, methyl alcohol, and carbon dioxide were the only substances produced. This decomposition,

$$(CH_3)_4N\cdot HCO_3 = (CH_3)_3N + CH_3\cdot OH + CO_2,$$

seemed to be nearly quantitative: 3 grams of the salt yielded 280 c.c. of carbon dioxide, the theoretical yield according to the above equation being about 500 c.c. Attempts were made to prepare the normal carbonate by dividing a solution of the base into two equal parts, saturating one with carbon dioxide, and then adding the other half to it. On evaporating, and leaving the salt for two months in a desiccator, a white, friable, crystalline, deliquescent salt was obtained. This salt, when heated, gave exactly the same results as the acid carbonate, and was probably a mixture of the acid carbonate with hydroxide of tetramethylammonium. Not a trace of carbonate of ethyl was produced. Possibly, therefore, the normal carbonate does not exist.

A few other salts were examined, the hydrosulphide, the acid sulphite, and the phosphate. The hydrosulphide is a very deliquescent salt, and when heated to about 200° easily decomposes into trimethylamine and methyl mercaptan. The acid sulphite crystallises fairly easily from concentrated solutions, and is not very deliquescent; on heating this salt, it melted at 180° and gave off some water of crystallisation, leaving a white salt behind; this did not melt or decompose till the temperature had risen above 300°, it then split up in a complicated manner, yielding trimethylamine, methyl alcohol, sulphur dioxide, and small quantities of a volatile, crystalline substance with a high boiling point, but it was not obtained in amount sufficient for purification. Traces also of sulphide of methyl were apparent.

The phosphate of tetramethylammonium is also a deliquescent salt. It was prepared by shaking a solution of the iodide with phosphate of silver; the solution thus obtained was strongly alkaline. With ammonium nitromolybdate, it gave a light-yellow precipitate which contained tetramethylammonium phosphate and molybdic acid. When the phosphate was heated at a very high temperature, it decomposed, giving trimethylamine and methyl alcohol which distilled, while metaphosphoric acid remained in the flask.

Conclusion.

It appears, therefore, that the action of heat on the salts of tetramethylammonium is usually of a simple nature, and trimethylamine is always produced. If the salt heated be one which decomposes at a low temperature, trimethylamine and a salt of methyl are the only substances produced. This is seen in the case of the fluoride, acetate, &c.,

$$(CH_3)_4NF = (CH_3)_3N + CH_3F;$$

but if the salt decomposes only at a high temperature, it is often the case that the salt of methyl (which is no doubt at first produced) is decomposed; for instance, the nitrite, oxalate, &c.

$$(CH_3)_4NNO_2 = (CH_3)_3N + (CH_3)NO_2,$$
$$4(CH_3)NO_2 = 2(CH_3)_2O + 4NO + O_2.$$

One salt alone decomposed in an unexpected manner, namely, the normal sulphate, but Crum-Brown and Blaikie (*loc. cit.*) have noticed that when the hyposulphite and sulphite of trimethylsulphine are heated, a similar splitting up of the molecule takes place—

$$(Me_3S)_2SO_3 = (Me_3S)MeSO_3 + Me_2S,$$
$$(Me_4N)_2SO_4 = (Me_4N)MeSO_4 + Me_3N.$$

It will be seen that the salts experimented with may be divided into two groups: firstly, those which are easily acted on by heat, and which decompose at a temperature of about 200°; secondly, those which are more stable, and are only decomposed at temperatures above 300°. Those belonging to the first class are the hydroxide, carbonate, acetate, benzoate, fluoride, and hydrosulphide; whilst those which belong to the second class are the iodide, bromide, chloride, oxalate, nitrate, &c.

Another point of interest is the solubility in water of the salts of tetramethylammonium, which seems to be in many cases exactly the reverse of the solubility of the ammonium salts, for the iodide of tetramethylammonium is the least soluble of the tetramethylammonium compounds with the halogens, the fluoride and chloride the most soluble. Amongst the other salts, the oxalate and sulphate are highly deliquescent, whilst the nitrate is scarcely even hygroscopic.

When the action of heat on the tetramethylammonium salts is compared with the action of that agent on the corresponding phosphorus and sulphur compounds, it is seen that the decomposition which they undergo is similar. This is shown in the case of the acetate—

$$(CH_3)_4N\cdot C_2H_3O_2 = (CH_3)_3N + CH_3\cdot C_2H_3O_2,$$
$$(CH_3)_3S\cdot C_2H_3O_2 = (CH_3)_2S + CH_3\cdot C_2H_3O_2,$$
$$(CH_3)_4P\cdot C_2H_3O_2 = (CH_3)_3PO + (CH_3)_2CO.$$

The apparent difference in decomposition which the phosphorus salt suffers is at once explained when we remember the intense affinity of that element for oxygen. Phosphorus, sulphur, and nitrogen are a group of elements which show a regular gradation in their affinity for oxygen and electronegative elements. When once phosphorus is

combined with oxygen, it is usually no easy matter to separate these two elements, consequently we find the method of decomposition of the tetramethylphosphonium salts containing oxygen differing in this respect from the corresponding ammonium compounds. The decomposition of the tetramethylphosphonium and the tetramethylammonium chlorides by heat also illustrates this difference—

$$2(CH_3)_4PCl = 2(CH_3)_3PHCl + C_2H_4,$$
$$(CH_3)_4NCl = (CH_3)_3N + CH_3Cl.$$

As sulphur does not possess such a strong attraction for oxygen as phosphorus, yet still possessing more than nitrogen for that element, we find that the sulphine salts resemble both the compound ammonium and phosphonium salts in their behaviour when heated.

XLVIII.—*Action of Heat on the Salts of Tetramethylphosphonium.*

By Norman Collie, Ph.D., F.R.S.E.

The action of heat on the salts of tetramethylphosphonium was undertaken partly to complete a series of experiments which had been made on the general method of decomposition of phosphonium salts when heated (*Phil. Mag.*, Aug., 1886, p. 183; *ibid.*, June, 1887, p. 27), and partly to compare their decomposition with that of the tetramethylammonium salts when similarly treated.

The iodide of tetramethylphosphonium was the starting point for the preparation of the other salts. It was prepared according to the method recommended by Hofmann (*Ber.*, **4**, 208); phosphonium iodide being heated with purified wood-spirit in sealed tubes at 180°. The iodide thus obtained was recrystallised from alcohol and ether. It gave no free phosphine when boiled with caustic soda, and a determination of iodine was made (58·9 per cent. and 58·7 per cent. iodine; theory for $(CH_3)_4NI$ = 58·2). The iodide when heated does not decompose easily, but at a temperature above 300° complicated decomposition occurs, free iodine and other products being formed.

Hofmann has already tried the action of heat on the hydroxide; he found that it split up into trimethylphosphine oxide and marsh-gas—

$$(CH_3)_4POH = (CH_3)_3PO + CH_4.$$

On repeating his experiment, the same result was obtained; 7 grams of the iodide were converted into hydroxide, and on heating this sub-

stance to a temperature of 115° complete decomposition occurred, 690 c.c. of gas were evolved, and a crystalline substance (trimethylphosphine oxide) remained in the flask. The gas proved to be pure methane (5·3 c.c. gave 5·2 c.c. of carbon dioxide), and the theoretical yield, according to the above equation, should be about 720 c.c. The trimethylphosphine oxide which remained in the flask was distilled. On redistillation, it was obtained as a highly crystalline and deliquescent substance; boiling point (corr.) 214—215°; melting point (corr.) 137—138°. Hofmann gives no analysis or melting or boiling point of this substance.

0·310 gram gave 0·440 CO_2 and 0·275 H_2O = 38·71 per cent. C and 9·85 per cent. H. Theory for $(CH_3)_3PO$ = 39·13 per cent. C and 9·78 per cent. H.

When mixed with chloride of platinum and hydrochloric acid, a chloroplatinate was obtained which crystallised from concentrated solutions, sometimes in magnificent orange plates, at other times in needle-shaped crystals.

I. 1·0945 gram heated at 90° lost 0·030 gram = 2·74 per cent. H_2O.

II. 0·583 gram gave 0·1635 Pt = 28·04 per cent. Pt.

III. 0·748 gram gave 0·204 Pt + 63·0 c.c. $AgNO_3$ (decinormal) = 27·27 Pt + 29·90 Cl.

IV. 0·352 gram gave 0·196 PO_2 + 0·141 H_2O = 15·18 per cent. C + 4·45 per cent. H_2O.

	Theory for $3Me_3PO,2HCl,PtCl_4,H_2O$.	Found. I.	Found. II.
C	15·34	15·18	—
H	4·40	4·45	—
Pt	27·89	27·27	28·04
Cl	30·20	29·90	—
H_2O	2·54	2·74	—

These results were unexpected, for the oxide of triethylphosphine and tribenzylphosphine give, with platinic chloride, chloroplatinates containing $4(C_2H_5)_3PO,H_2PtCl_6$ and $4(C_7H_7)_3PO,H_2PtCl_6$.

Action of Heat on Chloride of Tetramethylphosphonium.

This salt was prepared by adding hydrochloric acid to a solution of the hydroxide till it was neutral. On evaporation, a very deliquescent crystalline salt was obtained which gave with chloride of platinum an insoluble chloroplatinate crystallising in glittering yellow octahedra. 8 grams of the chloride were heated: the salt did not

melt till the temperature was above 300°, and it did not decompose till the bottom of the flask was hot enough to colour the Bunsen flame yellow. Eventually 800 c.c. of gas were collected and a solid crystalline substance had distilled. The gas consisted almost entirely of ethylene; an analysis of it was made, when 8·5 c.c. gave 16·5 c.c. of carbon dioxide, and the remainder was nearly all absorbed by bromine, giving a liquid b. p. 132·4°, and which was therefore dibromethylene. The crystalline solid was soluble in water and had an acid reaction. It contained chlorine, and when treated with caustic soda trimethylphosphine was liberated as an oily liquid which rapidly volatilised on warming, and caught fire at the mouth of the tube. The chloride therefore decomposes as follows:—

$$2(CH_3)_4PCl = 2(CH_3)_3HPCl + C_2H_4,$$

probably methylene is first produced during the decomposition of the chloride, but at once polymerises and becomes ethylene.

Action of Heat on Sulphate of Tetramethylphosphonium.

The sulphate was prepared by the action of sulphate of silver on iodide of tetramethylphosphonium. The excess of sulphate of silver which had dissolved was precipitated by the careful addition of sulphuretted hydrogen, and the solution was then made neutral with a small quantity of the hydroxide. On evaporation, a very deliquescent salt was obtained, which crystallised in thick needles. When mixed with a concentrated solution of aluminium sulphate and allowed to stand, no octahedral crystals could be obtained, or any double salt which seemed at all like an alum.

When heated, the solid sulphate decomposed at a temperature above 300°, only just melting, and much charring occurred. The distillate was crystalline and when treated with a little water did not entirely dissolve. The aqueous solution was separated from the crystals, and when redistilled gave pure oxide of trimethylphosphine, b. p. 214·5°, and m. p. 137·8°. The crystals which had been separated from the trimethylphosphine oxide proved to be the sulphide of trimethylphosphine. They melted at 105°, and when boiled with water rapidly volatilised; when warmed with a solution of a silver salt, they gave a black metallic mirror of silver sulphide.

Action of Heat on Benzoate of Tetramethylphosphonium.

This was made by neutralising a solution of the base with benzoic acid. This salt was also very soluble in water, and when obtained in

the crystalline condition it rapidly deliquesced if left in contact with the air. 20 grams of this salt were heated, but no decomposition occurred below 250°, and between that temperature and 300° the whole of the contents of the flask distilled over. During the decomposition, a little gas was formed which was chiefly carbon dioxide. In the receiver, a highly crystalline substance collected, which when treated with water dissolved and formed two layers which were separated. The lower layer proved to be an aqueous solution of trimethylphosphine oxide which on redistillation gave 8 grams of nearly pure oxide of trimethylphosphine (b. p. 214·5°), whilst the upper layer contained traces of trimethylphosphine and toluene, but when distilled the thermometer rose almost at once to 190°, and the whole of the substance passed over between that temperature and 210°. On redistillation most of it passed over at a temperature near 200° and seemed to consist of methyl phenyl ketone (b. p. 200°). Methyl phenyl ketone, however, is a solid which melts at 20°. The fraction 199—202° could not be made to solidify till it was cooled below 0°, and the crystals so formed melted again below 10°. The substance was unchanged when boiled with caustic soda solution, (and therefore was not methyl benzoate), when oxidised with chromic acid solution, it yielded formic and benzoic acids. From the above results, the benzoate decomposes almost completely as follows :—

$$(CH_3)_4P\cdot COOC_6H_5 = (CH_3)_3PO + CH_3\cdot COC_6H_5,$$

while a small portion decomposes—

$$(CH_3)_4P\cdot COOC_6H_5 = (CH_3)_3PO + CO_2 + C_6H_5\cdot CH_3.$$

Several other salts were experimented with, but as their method of decomposition is similar to that of the same salts of tetrethylphosphonium, only a short account of them is necessary.

The acetate when heated decomposed in a manner similar to the benzoate, chiefly into trimethylphosphine oxide and acetone; traces of ethyl acetate and trimethylphosphine were also observed.

The acid carbonate decomposed at a temperature a little above 100° into trimethylphosphine oxide, carbon dioxide, and methane. When the salts of tetramethylphosphonium are compared with the salts of tetrethylphosphonium, they show great similarity in their method of decomposition by heat, but owing to the greater stability of the methyl-group, the changes effected by the heating are not so complicated. The chief decomposition is always (in the case of oxy-salts) into the oxide of trimethylphosphine, sometimes accompanied by a ketone, sometimes, as in the case of the sulphate, by other products. This change was first pointed out as occur-

ring, in the paper by Professor Letts and the author (*loc. cit.*), on the tetrethylphosphonium salts. But it is more clearly seen, and the decomposition occurs more neatly, when the tetramethylphosphonium salts are heated. The decomposition of tetramethylphosphonium chloride resembles that of the tetrethylphosphonium salt, whilst the decomposition of the sulphate into the sulphide and oxide of trimethylphosphine exactly resembles the decomposition of the sulphate of tetrethylphosphonium. The comparison with the tetramethylammonium salts has already been made in the paper by Dr. Lawson and the author in the preceding paper.

XLIX.—*Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption-spectra.* (Part IX.) *On Isomeric Cresols, Dihydroxybenzenes, and Hydroxybenzoic Acids.*

By W. N. Hartley, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

Samples of the ortho-, meta-, and para-cresols, and of hydroquinone (quinol), pyrocatechol, and resorcinol were obtained from Mr. Kahlbaum's agents. Although they were found to be satisfactory after a single purification, nevertheless these specimens were redistilled and rendered free from any slight colour which they might have acquired by keeping, the final distillation being performed just previous to their examination. The distillates from the para- and ortho-cresols appeared quite colourless just at the moment of condensation, but at the lower end of the condensing tube they were observed to be pale yellow in colour, in other words, though colourless when hot these substances were coloured when cold. The meta-cresol became slightly coloured after keeping for some time. The three bodies stand in the following order as to colour :—

Metacresol, colourless.
Paracresol, yellow.
Orthocresol, darker yellow.

The specimens of salicylic acid, metahydroxybenzoic acid, and parahydroxybenzoic acid, the spectra of which were described in the *Philosophical Transactions*, Part I, 1879, were also examined by the method which I have more recently described. It was deemed advisable to recrystallise the two latter substances. They were accordingly dissolved by boiling in water; both formed somewhat brown solutions. Crystals from the solutions were carefully selected, washed free from mother-liquor and recrystallised as often as it appeared that they gave a slight tinge of colour to the liquid in which they were dissolved. Finally, they were obtained quite free from admixture with other crystals or uncrystallisable matter, and appeared as nearly as possible of perfect whiteness, yielding solutions quite free from any perceptible colour. The strength of the solutions photographed, as in cases latterly described, were molecular proportions in milligrams dissolved in 20 c.c. of alcohol. The descriptions of spectra and the molecular absorption curves are presented with this note.

So far the law of absorption of rays which it was expected would guide us in the orientation of the substituted hydrogens in the benzene nucleus does not appear to be the same for the hydrocarbons as for the cresols and dihydroxybenzenes.

In the hydroxybenzoic acids, the order of maximum absorption is the reverse of what it is in the xylenes.

Thus the oscillation frequencies of the most extreme rays transmitted by a milligram-molecule of the four classes of isomeric substances are the following:—

Oscillation Frequencies of the most Refrangible Rays transmitted by a Milligram-molecule.

Xylenes.		Cresols.		Dihydroxybenzenes.		Hydroxybenzoic acids.	
Ortho..	3611	Meta ..	3433	Meta ..	3466	Para ..	3359
Meta ..	3580	Ortho..	3413	Ortho..	3399	Meta..	3080
Para ..	3537	Para ..	3359	Para ..	3151	Ortho.	2986

In the case of the hydrocarbons, cresols, and dihydroxybenzenes, the 1 : 4 derivatives exercise the greatest absorption. Though they differ from the xylenes, the cresols and dihydroxybenzenes follow the same order of transparency; but the hydroxybenzoic acids altogether reverse the order of the xylenes, and differ from the cresols and dihydroxybenzenes.

We may assume that the absorption of rays manifested by one of any three isomerides is a measure of its rate of vibration, and consequently of the dissipation of energy resulting in the formation of the molecule. Hence the following classification is deduced:—

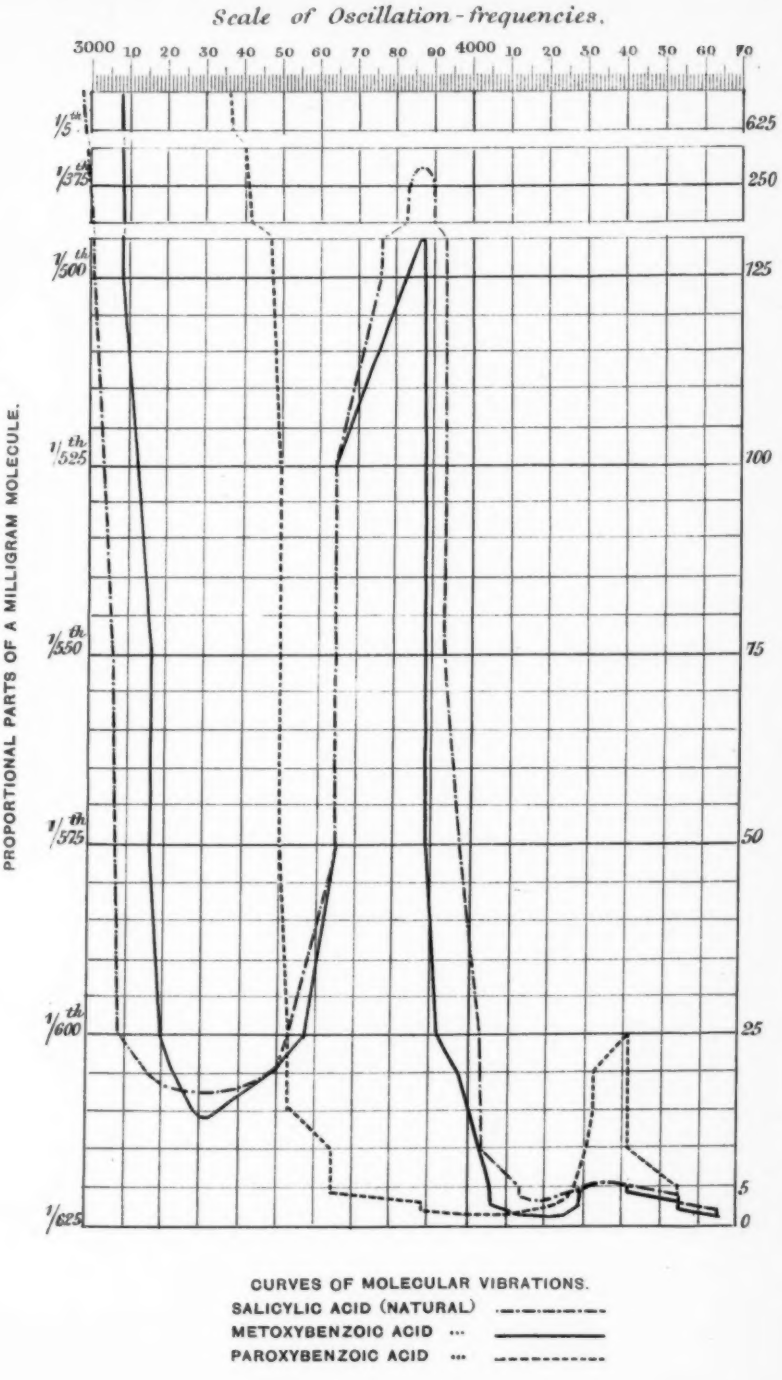
Dissipation of Energy during Formation.

	Least.		Greatest.
Xylenes	Para	meta	ortho
Cresols	Para	ortho	meta
Dihydroxybenzenes	Para	ortho	meta
Hydroxybenzoic acids....	Ortho	meta	para

In the *J. pr. Chem.*, **22**, 1—45, v. Rechenberg has given an account of the heat of combustion of the three hydroxybenzoic acids. The substance which evolves the largest amount of heat on combustion must be that by which the least amount of energy was dissipated during its formation, and it is worthy of remark that according to v. Rechenberg the hydroxybenzoic acids follow the order of classification given above, namely, ortho, meta, para, the heat units evolved being* 759,000, 754,000, and 752,000 respectively.

For the curves and measurements of the three xylenes see Trans., 1885, **48**, 702—749. For explanations of the plates see Trans., 1887, **51**, 201.

* These numbers are taken from Pattison-Muir's *Elements of Thermal Chemistry*, p. 65. Macmillan, 1885.



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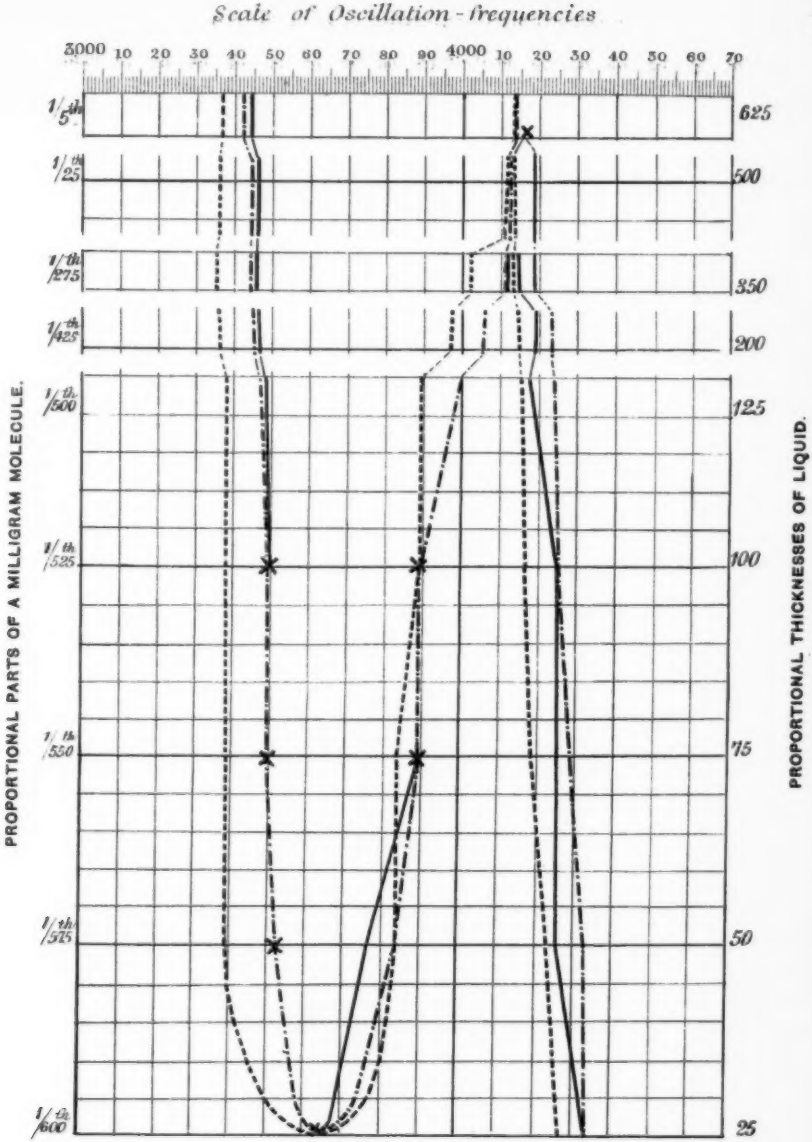
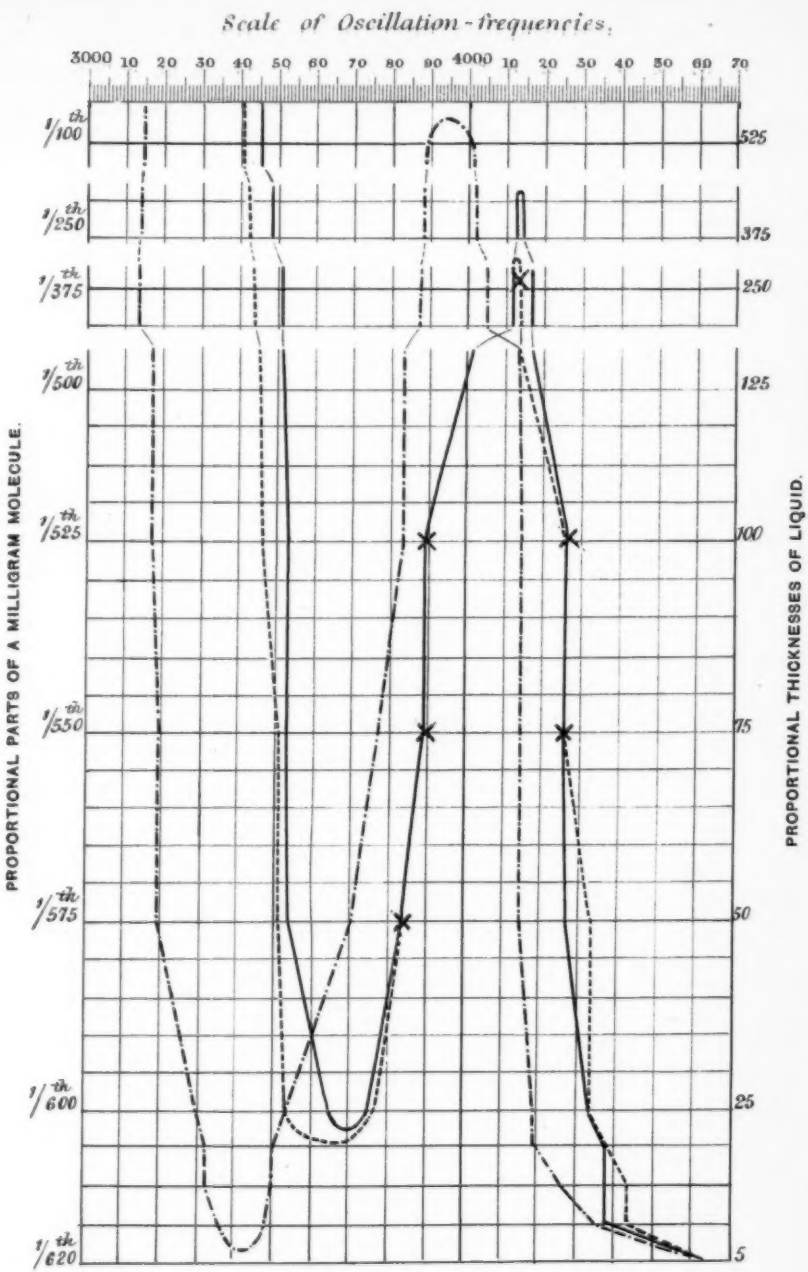


CURVES OF MOLECULAR VIBRATIONS.

ORTHO CRESOL ··· -·-·-·-



CURVES OF MOLECULAR VIBRATIONS.

QUINOL ... ... 1.4.
PYROCATECHOL ... ... 1.2.
RESORCINOL ... ... 1.3.

The curves of Pyrocatechol and Resorcinol run one into the other at the points marked thus X

ORTHOCRESOL, $C_6H_4(CH_3)\cdot OH$ 1 : 2. 0·108 gram in 20 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3413	2930	3439	2906·5		
Absorption band from	3413 to 4125	2930 to 2424·3	3439 to 4125	2906·5 to 2424·3		
Two very feeble lines at.....	4125	2424·3	—	—	Same as last.	
" "	4136	2418	—	—		
Feeble spectrum to.....	—	—	4185	2390		
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	3460	2890·3	3480	2875	—	—
Absorption band from	3460 to 4093	2890·3 to 2444	3480 to 4016	2875 to 2490	—	—
Feeble spectrum to.....	4232	2364	—	—	—	—
Faint spectrum to.....	—	—	4253	2352	—	—

ORTHOCRESOL—*continued.* 0·108 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3493	2863	3493	2863	3493	2863
Absorption band from	3493 to 4016	2863 to 2490	3493 to 3890	2863 to 2568	3493 to 3890	2863 to 2568
Faint spectrum to.....	4253	2352	4253	2352	—	—
Weak spectrum to.....	—	—	—	—	4291	2331·5

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	3525	2836·5	3531	2831·5	—	—
Absorption band from	3525 to 3832	2836·5 to 2609	—	—	—	—
			(Absorption band still visible, but rays are transmitted *very feebly* between wave-lengths 2831 and 2653.)			
Very feeble spectrum to..... ...	—	—	3768	2653	—	—
Weak spectrum to.....	4331	2310	4331	2310	—	—

ORTHOCRESOL—*continued.* 0·108 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3531	2831·5	Same as last.		4374·4	2286
Very feeble spectrum to.....	3768	2653			—	—
Weak spectrum to.....	4331	2310			—	—
But feeble to	—	—			3768	2653
Thickness of layer of liquid.....	**2 mm.**		**1 mm.**			
Continuous spectrum to...	4426·7	2259	4426·7	2259	—	—
But faint to.....	3768	2653	—	—	—	—
Spectrum extends to.....	—	—	4660	2145·9	—	—

METACRESOL, $C_6H_4(CH_3)\cdot OH$ 1 : 3. 0·108 gram in 20 c.c. alcohol. Sp. gr. 8.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3433	2912·5	3460	2890·3		
Absorption band from.....	3433 to 4125	2912·5 to 2424·3	3460 to 4125	2890·3 to 2424·3		
Two very feeble lines at.....	4125	2424·3	—	—	Same as last.	
" "	4136	2418	—	—		
Two weak lines at.....	—	—	4125	2424·3		
" "	—	—	4136	2418		

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	3460	2890·3	3493	2863	—	—
Absorption band from	3460 to 4125	2890·3 to 2424·3	3493 to 4016	2863 to 2490·5	—	—
Spectrum extends feebly to.....	4190	2387	4190	2387	—	—

METACRESOL—*continued.* 0·108 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to.....	3493	2863	3493	2863	3493	2863
Absorption band from.....	3493 to 3890	863 to 2568	3493 to 3890	2863 to 2568	3493 to 3832	2863 to 2609
Spectrum extends to.....	4190	2387	4253	2352	4253	2352

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3525	2836·5	3531	2836·5	—	—
Absorption band from	3525 to 3768	2836·5 to 2653	—	—	—	—
Feeble spectrum to.....	—	—	3768	2653	—	—
Spectrum extends to....	4253	2352	4331	2310	—	—

METACRESOL—*continued.* 0·108 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.	3 mm.
Continuous spectrum to.....	3531	2836·5	Same as last.	Same as last.
Feeble spectrum to.....	3768	2653		
Spectrum extends to.....	4331	2310		

Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	4426·7	2259	4660	2145·9	—	—

PARACRESOL, $C_6H_4(CH_3)\cdot OH$ 1 : 4. 0·108 gram in 20 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3359	2976·5			3359	2976·5
Absorption band from	3359 to 4125	2976·5 to 2424·3			3359 to 4016	2976·5 to 2490·5
Two very feeble lines at.....	4125	2424·3	Same as last.		—	—
" "	4136	2418			—	—
Spectrum extends to.....	—	—			4136	2418

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	Same as last.		3392	2948	—	—
Absorption band from			3392 to 3890	2948 to 2658	—	—
Spectrum extends to			4163	2402	—	—

PARACRESOL—*continued.* 0·108 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to	3392	2948			3392	2948
Absorption band from	3392 to 3890	2948 to 2658	Same as last.		3392 to 3832	2948 to 2609
Spectrum extends to.....	4185	2390			4185	2390

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3392	2948	3426	2918·5	—	—
Absorption band from	3392 to 3832	2948 to 2609	—	—	—	—
Very feeble spectrum to.....	—	—	3768	2653	—	—
Spectrum extends to.....	4232	2364	4253	2352	—	—

PARACRESOL—*continued.* 0·108 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to.....	3426	2918·5	Same as last.		—	—
Very feeble spectrum to.....	3768	2653			—	—
Spectrum extends to.....	4253	2352			4331	2310
Thickness of layer of liquid.....	**2 mm.**		**1 mm.**			
Spectrum extends to.....	4331	2310	4660	2145·9	—	—

PYROCATECHOL, $C_6H_4(OH)_2$ 1 : 2. 0·110 gram in 20 c.c. OH_2.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to...	3399	2942	3413	2930	3426	2918·5
Thickness of layer of liquid.....	**2 mm.**		**1 mm.**			
Continuous spectrum to...	3439	2906·5	3460	2890·3	—	—
Absorption band from	3439 to 4125	2906·5 to 2424·3	3460 to 4016	2890·3 to 2490·5	—	—
Two weak lines at.....	4125	2424·3	—	—	—	—
„ „	4136	2418	—	—	—	—
Weak spectrum to.....	—	—	4136	2418	—	—

PYROCATECHOL—*continued.* 0·110 gram in 100 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.	
Continuous spectrum to	3460	2890·3	3460	2890·3	3507	2852·3
Absorption band from	3460 to 4016	2890·3 to 2490·5	3460 to 3890	2890·3 to 2568	3507 to 3890	2852·3 to 2568
Weak spectrum to.....	4136	2418	4253	2352	4253	2352

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3507	2852·3	3531	2831·5	—	—
Absorption band from	3507 to 3832	2852 3 to 2609	3531 to 3768	2831·5 to 2653	—	—
Weak spectrum to.....	4331	2310	4331	2310	—	—

PYROCATECHOL—*continued.* 0·110 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to.....	3531	2831·5	3531	2831·5	3580	2793
Absorption band from	3531 to 3768	2831·5 to 2653	—	—	—	—
Faint spectrum to.....	—	—	3768	2653	3768	2653
Weak spectrum to..... ..	4331	2310	4374·4	2286	4426·7	2259

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	Same as last but stronger.		4426·7	2259	—	—
Very faint to			4660	2145·9	—	—

RESORCINOL, $C_6H_4(OH)_2$ 1 : 3. 0·110 gram in 20 c.c. OH_2.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3466	2885	3466	2885	3487	2869
Absorption band from	—	—	—	—	3487 to 4125	2869 to 2424·3
Two faint lines at.....	—	—	—	—	4125	2424·3
„ „	—	—	—	—	4136	2418

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	3507	2852·3	3507	2852·3	—	—
Absorption band from	3507 to 4125	2852·3 to 2424·3	3507 to 4016	2852·3 to 2490·5	—	—
Two weak lines at.....	4125	2424·3	—	—	—	—
„ „	4136	2418	—	—	—	—
Weak spectrum to.....	—	—	4163	2402	—	—

RESORCINOL—*continued.* 0·110 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to.....	3507	2852·3	3531	2831·5	3531	2831·5
Absorption band from.....	3507 to 4016	2852·3 to 2490·5	3531 to 3890	2831·5 to 2568	3531 to 3890	2831·5 to 2568
Weak spectrum to.....	4163	2402	4253	2352	4253	2352

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3537	2826·5	3537	2826·5	—	—
Very faint to	—	—	3647	2740	—	—
Absorption band from.....	3537 to 3832	2826·5 to 2609	3647 to 3768	2740 to 2653	—	—
Weak spectrum to.....	4253	2352	4331	2310	—	—

RESORCINOL—*continued.* 0·110 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.	
Continuous spectrum to	3537	2826·5	3580	2793		
Very faint to	3647	2740	—	—		
Faint spectrum to	—	—	3768	2653	Same as last; a little stronger	
Absorption band from	3647 to 3768	2740 to 2653	—	—		
Weak spectrum to.....	4331	2310	4374·4	2286		

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to	3580	2793	4426·7	2259	—	—
Faint spectrum to.....	3768	2653	4660	2145·9	—	—
Weak spectrum to.....	4374·4	2286	—	—	—	—

Quinol, $C_6H_4(OH)_2$ 1 : 4. 0·110 gram in 20 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to.....	3151	3171	3151	3171	3151	3171
Absorption band from	—	—	3151 to 3890	3171 to 2568	3151 to 3890	3171 to 2568
Very feeble discontinuous to	—	—	4033	2479·5	—	—
Faint discontinuous to	—	—	—	—	4033	2479·5

Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to.....	3151	3171	3187	3140	—	—
Absorption band from	3151 to 3890	3171 to 3568	3187 to 3832	2609	—	—
Weak discontinuous to.....	4050	2469·5	—	—	—	—
Continuous spectrum to.....	—	—	4125	2424·3	—	—

Quinol. 0·110 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to	3187	3140	3187	3140	3194	3130
Absorption band from	3187 to 3832	3140 to 2690	3187 to 3832	3140 to 2690	3194 to 3768	3130 to 2653
Continuous spectrum to.....	4125	2424·3	4136	2418	4136	2418

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous spectrum to	3194	3130	3221	3104·5	—	—
Absorption band from	3194 to 3701	3130 to 2701	3221 to 3647	3104·5 to 2740	—	—
Continuous spectrum to	4136	2418	4136	2418	—	—

QUINOL. 0·110 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Continuous spectrum to	3297	3033	3320	3014	3320	3014
Absorption band from	3297 to 3531	3033 to 2831·5	3320 to 3500	3014 to 2857·5	3320 to 3500	3014 to 2857·5
Continuous spectrum to	4190	2387	4190	2387	4253	2352
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous spectrum to	3359	2976·5	—	—	—	—
Absorption band	3359 to 3493	2976·5 to 2863	—	—	—	—
Spectrum extends to.....	4331	2310	4660	2145·9	—	—

SALICYLIC ACID, $C_6H_4(OH)\cdot COOH$ 1 : 2. From Oil of Wintergreen. 0·138 gram in 20 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation-frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	2986·5	3348·5	2986·5	3348·5	3008·5	3324
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	3008·5	3324	3008·5	3324	—	—
Absorption band from	3008·5 to 3826	3324 to 2613	3008·5 to 3757	3324 to 2662	—	—
Rays transmitted to	3890	2568	3925	2545	—	—

SALICYLIC ACID—*continued.* 0·138 gram in 100 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	3008·5	3324	3044	3283	3066	3261
Absorption band from	3008·5 to 3757	3324 to 2662	3044 to 3641	3283 to 2744·5	3066 to 3641	3261 to 2744·5
Rays transmitted to	3925	2545	3925	2545	3925	2545

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	3066	3261	3080	3245·5	—	—
Absorption band from	3066 to 3641	3261 to 2744·5	3080 to 3525	3245·5 to 2836·5	—	—
Rays transmitted to.....	3970	2518	4028	2482·5	—	—

SALICYLIC ACID—*continued.* 0·138 gram in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to	3080	3245·5	3151	3171	4033	2479·3
Absorption band from	3080 to 3525	3245·5 to 2836·5	3151 to 3494	3171 to 2863	—	—
Rays transmitted to	4028	2482·5	4033	2479·5	—	—

Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	4033	2479·5	4130	2421	—	—
Absorption band from	—	—	4130 to 4326	2421 to 4313	—	—
Rays transmitted to.....	—	—	4415	2265	—	—

SALICYLIC ACID—*continued*. 0·138 gram in 2500 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	4130	2421	4130	2421	4550	2197
Absorption band from	4130 to 4326	2421 to 2313	4130 to 4243	2421 to 2358	—	—
Rays transmitted to	4415	2265	4550	2197	—	—
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	4658	2148·5	4658	2148·5	—	—

The solution 0·138 gram in 20 c.c. gave a brilliant blue fluorescence, decreasing according as the solution was diluted.

METAHYDROXYBENZOIC ACID, $C_6H_4(OH)\cdot COOH$, 1 : 3. 0·138 gram in 20 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	3080	3245·5	3080	3245·5	3080	3245·5

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	3080	3245·5	3080 to 3826	3245·5	—	—
Absorption band from	—	—	3885	3245 to 2613	—	—
Rays transmitted to	—	—	3885	2572	—	—

METAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 100 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	3080	3245·5	3115	3208	3151	3171
Absorption band from	3080 to 3826	3245·5 to 2613	3115 to 3641	3208 to 2744·5	3151 to 3641	2171 to 2744·5
Rays transmitted to	3885	2572	3885	2572	3885	2572
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	Same as 3 mm.		3187	3140	—	—
Absorption band from			3187 to 3568	3140 to 2802·5	—	—
Rays transmitted to			3914	2553	—	—

METAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 500 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	3187	3140	3221	3104·5	3270	3059
Absorption band from.....	3187 to 3568	3140 to 2802·5	3221 to 3494	3104·5 to 2863	3270 to 3359	3059 to 2976·5
Rays transmitted to	3914	2553	3970	2518	3999	2500·5
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	4028	2482·5	4055	2466	—	—
Absorption band from	—	—	4055 to 4311	2466 to 2321	—	—
Rays transmitted to	—	—	4420	2263	—	—

METAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 2500 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	4055	2466	4055	2466	4055	2466
Absorption band from	4055 to 4311	2466 to 2321	4055 to 4311	2466 to 2321	4055 to 4297	2466 to 2329
Rays transmitted to	4420	2263	4420	2263	4555	2195

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	4082	2450	4658	2148·5	—	—
Absorption band from	4082 to 4297	2450 to 2329	—	—	—	—
Rays transmitted to	4555	2195	—	—	—	—

Slight blue fluorescence.

PARAHYDROXYBENZOIC ACID, $C_6H_4(OH)\cdot COOH$, 1 : 4. 0·138 gram in 20 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	3359	2976·5	3359	2976·5	3392	2949
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	3426	2918·5	3480	2875	—	—

PARAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 100 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	3480	2875	3500	2857·5	3500	2857·5
Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	3500	2857·5	3525	2836·5	—	—
Absorption band from	—	—	3525 to 4415	2836·5 to 2265	—	—

PARAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 500 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.
Spectrum extends to.....	3525	2836·5	3525	2836·5	Same as 4 mm.
Absorption band from	3525 to 4415	2836·5 to 2265	3525 to 4326	2836·5 to 2313	
Rays transmitted to	—	—	4415	2265	

Thickness of layer of liquid.....	2 mm.		1 mm.			
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	3641	2744·5	3641	2744·5	—	—
Absorption band from	3641 to 4306	2744·5 to 2323·5	3641 to 4297	2744·5 to 2329	—	—
Rays transmitted to	4415	2265	4550	2197	—	—

PARAHYDROXYBENZOIC ACID—*continued.* 0·138 gram in 2500 c.c. Alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
Spectrum extends to.....	3641	2744·5	Same as 5 mm.		3885	2572
Absorption band from	3641 to 4297	2744·5 to 2329			3885 to 4297	2572 to 2329
Rays transmitted to	4550	2197			4550	2197

Thickness of layer of liquid.....	2 mm.		1 mm.			
Spectrum extends to.....	3885	2572	4658	2148·5	—	—
Absorption band from	3885 to 4179	2572 to 2393	—	—	—	—
Rays transmitted to	4658	2148·5	—	—	—	—

L.—*Proof of the Identity of Natural and Artificial Salicylic Acid.*

By W. N. Hartley, F.R.S.

As it appears to be a matter of some importance, from a medical point of view, to determine whether the salicylic acid from phenol is identical with that from oil of winter-green, there being some doubt upon the subject, I have made an examination of both with the object of setting this matter beyond question.

Two samples of salicylic acid, one prepared from oil of winter-green and the other by Kolbe's process from phenol, were submitted to recrystallisation by Messrs. Hopkin and Williams until it was found that they both crystallised in prisms 10 mm. in length and 1 mm. in thickness. Both specimens have a silky lustre, but they are not perfectly white, their tint being cream-coloured. When these two products were shown to me, I purchased a sample of each for the purpose of examination. Molecular proportions of these crystals were dissolved in 20 c.c. of alcohol, and the spectra of various thicknesses of liquid were photographed. The two series of photographs were identical in every particular, and hence they yield exactly the same curve, which is a searching test of the identity of the two substances.

It appears to be an established fact that recrystallised commercial salicylic acid can be obtained in a state of great purity and identical with that from oil of winter-green.

LI.—*Researches on the Constitution of Azo- and Diazo-derivatives.* IV. *Diazoamido-compounds* (continued).

By Raphael Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

In former papers on the diazoamido-compounds (*Chem. Soc. Trans.*, 1886, 624; 1887, 102 and 434), it has been shown that the alkyl-derivatives of *mixed* compounds* of the general formula $X{\cdot}N_2R'{\cdot}Y$ are apparently capable of existing in three isomeric modifications:—

* This designation is applied to all diazoamido-compounds in which the two radicles are dissimilar (*Phil. Mag.*, June, 1887, 518), and is not restricted, as in a recently published paper (*Ber.*, 1888, 1016), to those compounds which contain one fatty and one aromatic radicle.

(1.) Produced by the action of diazotised $X{\cdot}NH_2$ upon $Y{\cdot}NHR'$.

(2.) Produced by the action of diazotised $Y{\cdot}NH_2$ upon $X{\cdot}NHR'$.

(3.) Produced by the direct alkylation of the mixed compound $X{\cdot}N_2H{\cdot}Y$.

As this fact is of the greatest interest in connection with the general subject of chemical isomerism, we have lately been concentrating our efforts on this branch of the work, with the object of investigating in the first place how far the isomerism in question can be regarded as holding good—whether, in fact, the isomerism is perfectly general whatever radicles may be represented by X, Y, and R′ in the above formulæ. In order to decide this point, it is evidently essential to prepare as many distinct triplets as possible, so that the individual influence of the different radicles may be studied. It is, moreover, obvious that at least two of the compounds out of each triplet should be solid, so that their identity or non-identity may be established by their melting points, as the instability of the diazoamido-compounds when heated does not permit of the boiling points of the oily compounds being determined.

The manifestly complicated practical requirements which have thus to be met must necessarily make the present branch of the investigation a very protracted one, because, in the first place, each pair of amines must be experimented with in order to see whether they can be combined so as to form a diazoamido-compound; and, in the next place, the alkyl-derivatives have to be prepared in order to see whether they satisfy the required conditions. As the nitranilines lent themselves most readily to the former investigations, the results of which have been made known in the papers previously referred to, we have continued our experiments with these nitroamines. Some practical points in the general method of working may here be alluded to before describing the results in detail.

All experience with the mixed diazoamido-compounds having shown us that the alkyl-derivative prepared by the third of the foregoing methods (direct alkylation) was the isomeride of lowest melting point, it has been found advantageous in all cases to prepare this compound first. If this last alkyl-derivative is solid, the two other isomerides will most probably be also solid. On the other hand, if the alkyl-derivative in question is oily, the two other modifications may or may not be solid, but they must be prepared in order to decide this point before the investigation of the triplet can be considered as complete. The nature of the practical difficulties which have to be overcome will be seen more fully in the course of the description of the experimental results.

1. *Methylation of the Compound (m. p. 211°) produced by the Action of Diazotised Paranitraniline on Metanitraniline or of Diazotised Metanitraniline on Paranitraniline.*

The first complete triplet of isomeric alkyl-derivatives described in our former papers was prepared from para- and meta-nitraniline and contained the radicle ethyl. In order to ascertain the effect of substituting another radicle for ethyl, the corresponding series of methyl-derivatives has been prepared. The mixed diazoamido-compound was dissolved in alcohol with the addition of the necessary quantity of potassium hydroxide (one molecular proportion), and the solution boiled in a flask with an upright condenser for about 10 hours with one molecular proportion of methyl iodide. The methyl-derivative separates out as a yellow crystalline deposit which is collected, washed with alcohol, and purified by several crystallisations from alcohol containing a few drops of caustic soda solution to insure the removal of any unmethylated compound. The purified substance forms small, bright yellow needles, very similar to the ethyl-derivative in appearance and properties, and having the same melting point, 148°. The following results were obtained on analysis :—

I. 0·1394 gram gave 0·2672 gram CO_2 and 0·0494 gram H_2O.
II. 0·1080 „ 0·2050 „ „ 0·0390 „
III. 0·1244 „ 25·4 c.c. moist N at 14° and 754·7 mm. bar.
IV. 0·1248 „ 24·4 „ „ 12° and 760·3 „

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2(CH_3){\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	II.	III.	IV.
C	51·83	52·27	51·76	—	—
H	3·65	3·93	4·01	—	—
N	23·25	—	—	23·24	23·20

The compound is readily decomposed by strong hydrochloric acid. On standing for about an hour at the ordinary atmospheric temperature under excess of strong acid, the substance gradually dissolves, leaving only a very slight residue; the acid solution contains a mixture of meta- and para-nitrobenzene diazochlorides and the two corresponding methylnitranilines. The decomposition is thus similar to that of the ethyl-derivative and of the mixed diazoamido-compound from which these alkyl-derivatives are obtained.

2. *Methylation of Paradinitro-diazoamidobenzene, m. p. 223°.*

The methyl-derivative of the above substance was prepared in the usual way, by dissolving the dinitrodiazo-compound in alcohol with

the theoretical quantity of potassium hydroxide and cohobating with the necessary quantity of methyl iodide. After purification by two or three crystallisations from alcohol, made slightly alkaline by caustic soda, the methyl-derivative was obtained in the form of small yellow needles melting at 219°:—

I. 0·1458 gram gave 0·2778 gram CO_2 and 0·0490 gram H_2O.
II. 0·1092 „ 0·2086 „ „ 0·0364 „
III. 0·1872 „ 36·4 c.c. moist N at 13·5° and 776·7 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	II.	III.
C	51·83	51·96	52·10	—
H	3·65	3·73	3·70	—
N	23·25	—	—	23·45

The substance is decomposed quite normally by acids. With excess of cold hydrochloric acid, it is resolved into paranitrodiazobenzene chloride and methylparanitraniline; hot hydrochloric acid produces paranitrochlorobenzene and methylparanitraniline.

3. *Methylation of Metadinitro-diazoamidobenzene, m. p.* 194°.

This methyl-derivative was prepared in the same manner as the others, and after purification by crystallisation from alcohol forms small yellow needles, paler in colour and rather more soluble in alcohol than the preceding modifications. The melting point is 127—128°, the pure substance giving the following results on analysis:—

I. 0·1740 gram gave 0·3302 gram CO_2 and 0·0584 gram H_2O.
II. 0·1740 „ 34 c.c. moist N at 15° and 766·3 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	II.
C	51·83	51·75	—
H	3·65	3·73	—
N	23·25	—	23·07

The compound is decomposed by cold hydrochloric acid into metanitrodiazobenzene chloride and methylmetanitraniline, and by hot acid into the same alkylnitraniline and metanitrochlorobenzene.

4. *The Action of Diazotised Paranitraniline on Methylmetanitraniline.*

Paranitraniline was diazotised in hydrochloric acid solution and added to an aqueous solution of the hydrochloride of methylmetanitraniline. If care is taken to have present only a minimum of acid,

the yellow diazo-compound commences to separate out immediately on mixing the solutions; if too much acid is used, the separation of the diazo-compound takes place very slowly, but can be promoted by the addition of sodium acetate. After standing for some hours, the mixed solutions become almost solid from the separation of a yellow crystalline pulp. The latter is collected, washed well with water, and purified in the usual way by crystallisation from alcohol, with the addition of a few drops of strong caustic soda solution. The pure substance resembles its isomerides in appearance and properties, forming small yellow needles melting at 168° :—

I. 0·1084 gram gave 0·2068 gram CO_2 and 0·0372 gram H_2O.
II. 0·1232 „ 24·6 c.c. moist N at 13·5° and 745·5 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2(CH_3){\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	Found. II.
C	51·83	52·02	—
H	3·65	3·81	—
N	23·25	—	23·08

The substance is decomposed by cold hydrochloric acid into paranitrodiazobenzene chloride and methylmetanitraniline, and by hot acid into the corresponding nitrochlorobenzene and the same alkylnitraniline.

5. *The Action of Diazotised Metanitraniline on Methylparanitraniline.*

This modification was prepared in a precisely similar manner to the last, the purified substance being obtained in the form of minute bright yellow needles melting at 176—177°:—

I. 0·1146 gram gave 0·2194 gram CO_2 and 0·0396 gram H_2O.
II. 0·1134 „ 22·4 c.c. N at 17·5° and 760·8 mm. bar.
III. 0·1434 „ 28 „ 14° „ 762·6 „

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2(CH_3){\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	Found. II.	Found. III.
C	51·83	52·21	—	—
H	3·65	3·83	—	—
N	23·25	—	22·98	23·04

The compound undergoes normal decomposition by hydrochloric acid, the hot acid giving metanitrochlorobenzene and methylparanitraniline, and the cold acid the last compound and metanitrodiazobenzene chloride.

The methyl-derivatives now described furnish a second complete

triplet of isomeric compounds, confirming the results obtained with the ethyl-derivatives. The isomerism will be seen from the melting points given in the following comparative table :—

Dinitrodiazoamido-compound.	Melting point of methyl-derivative.	Melting point of ethyl-derivative.
1. Alkylation of the compound produced by the action of diazotised paranitraniline on metanitraniline, or *vice versâ*	148°	148°
2. Action of diazotised metanitraniline on alkyl-paranitraniline	176—177°	174—175°
3. Action of diazotised paranitraniline on alkyl-metanitraniline	168°	187°
4. Alkylation of the compound produced by the action of diazotised paranitraniline on paranitraniline	219°	191—192°
5. Alkylation of the compound produced by the action of diazotised metanitraniline on metanitraniline	127—128°	119°

The compounds 4 and 5 in the preceding table are normal, that is, not mixed compounds, but are added in order to complete the list of isomerides as far as our present experiments have extended.

In the course of our search for triplets of isomeric alkyl-derivatives having at least two solid members, several new diazoamido-compounds and their alkyl-derivatives have been prepared, and descriptions of these are now subjoined.

6. *Dinitrodibromo-diazoamidobenzene.*

Paranitro-orthobromaniline [$NO_2 : Br : NH_2 = 1 : 3 : 4$, m. p. 104°], was dissolved in alcohol, with the addition of a little dilute hydrochloric acid, and the necessary quantity of sodium nitrite dissolved in a small quantity of water added to the cold solution. The yellow, flocculent, diazoamido-compound commences to separate out at once, and after standing for eight hours the separation is completed by diluting the solution with a large bulk of cold water. The product was collected, washed with water, and crystallised from hot alcohol, in which the substance dissolves but slightly. Analysis having shown the compound to be impure, it was crystallised two or three

times from a mixture of alcohol and toluene, and was finally obtained in the form of hair-like, orange needles, which separated from the solution in rosettes. The melting point is 202°.

0·1435 gram gave 0·1207 gram AgBr.

	Calculated for $NO_2 \cdot BrC_6H_3 \cdot N_2H \cdot C_6H_3Br \cdot NO_2$.	Found.
Br	35·95	35·79

The substance is strongly acid, dissolving in hot aqueous alkalis or in cold alcoholic alkali with a fine crimson colour.

The bromonitraniline from which this compound is obtained possesses but very feeble basic properties, and is thus almost insoluble in acids. For this reason, it is difficult to diazotise or to make it react with other diazo-chlorides without the use of alcohol as a solvent. This bromonitraniline did not appear, therefore, to be well adapted for the present inquiry, and the experiments were discontinued.

7. *Paradichlorodiazoamidobenzene and its Ethyl-derivative.*

Parachloraniline is dissolved in water containing just enough hydrochloric acid to keep the base dissolved in the cold (about 20 grams of the base to 1 litre of water and acid) and the necessary quantity of sodium nitrite (1 mol. to 2 mols. of the base) dissolved in water is gradually added to the cold solution. The diazoamido-compound soon begins to separate as an ochreous precipitate, and the separation is completed by adding a quantity of sodium acetate equivalent to the hydrochloric acid used. After being collected and washed, the substance was crystallised from dilute alcohol, and finally from a mixture of benzene and petroleum, when it was obtained in the form of ochreous needles melting at 130°.

I. 0·1144 gram gave 0·2263 gram CO_2 and 0·0353 gram H_2O.
II. 0·1382 „ 0·1485 „ AgCl.
III. 0·2164 „ 28·5 c.c. moist N at 12·5° and 749·7 mm. bar.

	Calculated for $C_6H_4Cl \cdot N_3H \cdot C_6H_4Cl$.	Found.		
		I.	II.	III.
C	54·13	53·94	—	—
H	3·42	3·42	—	—
N	15·79	—	—	15·38
Cl	26·69	—	26·56	—

The compound is decomposed normally by cold hydrochloric acid into parachloraniline and parachloro-diazobenzene chloride.

A silver salt was prepared by adding an ammoniacal solution of silver nitrate to an alcoholic solution of the substance containing a little ammonia. The salt is at once precipitated as a yellow jelly, which slowly changes to a crystalline condition, the crystals appearing under the microscope in the form of fine yellow needles. After being washed with alcohol and dried, the salt was analysed, the silver and chlorine approximating to the formula $C_6H_4Cl\cdot N_2Ag\cdot C_6H_4Cl$, and the C, H, and N agreeing somewhat more closely with the calculated numbers:—

I. 0·2454 gram gave 0·3552 gram CO_2 and 0·0532 gram H_2O.
II. 0·0986 „ 9·4 c.c. N at 15·5° and 767 mm. bar.

	Calculated for $C_{12}H_8Cl_2N_2Ag$.	Found. I.	Found. II.
C	38·60	39·47	—
H	2·14	2·41	—
N	11·26	—	11·24

The difficulty of purifying and analysing these explosive metallic derivatives of the diazoamido-compounds has been alluded to in a former paper (Trans. 1887, 445).

The ethyl-derivative is prepared in the usual way by boiling a solution of the substance in (absolute) alcohol with the necessary quantities of potassium hydroxide and ethyl iodide. After cohobating for 1—2 hours, the alcohol is distilled off and the contents of the flask diluted with water, when the ethyl-derivative separates out as an oil which, on standing for two or three days, solidifies to an ochreous resinous mass. The latter is dissolved in dilute alcohol, boiled with animal charcoal and filtered, when the purified substance separates out on cooling in the form of flat, straw-coloured needles having a melting point of 85·5°. Two crystallisations from dilute alcohol were necessary before the substance was quite pure:—

I. 0·1206 gram gave 0·2532 gram CO_2 and 0·050 gram H_2O.
II. 0·1090 „ 13·2 c.c. N at 12·5° and 771 mm. bar.
III. 0·1663 „ 0·1612 gram AgCl.

	Calculated for $C_6H_4Cl\cdot N_2(C_2H_5)\cdot C_6H_4Cl$.	Found. I.	Found. II.	Found. III.
C	57·14	57·26	—	—
H	4·42	4·60	—	—
N	14·28	—	14·55	—
Cl	24·14	—	—	23·97

The substance is decomposed by cold hydrochloric acid into parachloro-diazobenzene chloride and ethylparachloraniline.

8. *Benzyl-derivatives of Diazoamido-compounds not containing Nitro-groups.*

The chief object in undertaking the next series of experiments was to find if possible a triplet of isomerides fulfilling the necessary conditions and not containing nitro-groups. The first attempt, in accordance with the general method of working already described, was made with the mixed compound obtained from aniline and para-toluidine. The substance was benzylated in alcoholic solution with benzyl chloride and potassium hydroxide in the usual way. On distilling off the alcohol and diluting the residue with water, the benzyl-derivative separates out as a dark, viscid oil which does not solidify on standing for weeks. An attempt was next made to prepare the isomeride by the action of diazotised paratoluidine on benzylaniline.* The latter was dissolved in hot dilute hydrochloric acid, and the solution when cold just neutralised with ammonia, the contents of the flask being strongly agitated so as to get the benzyl-aniline into the state of an emulsion. The solution of diazotoluene chloride was then added to the benzylaniline emulsion and the mixture allowed to stand for about 12 hours. The ochreous deposit was collected and washed, but soon began to agglomerate into an oil, and microscopic examination revealed the fact that the precipitate which at first sight appeared solid was really an emulsion of viscid oily globules with the aqueous liquid. It appears, therefore, that the triplet of mixed diazoamido-compounds comprised under the formula $C_6H_5{\cdot}N_3(C_7H_7){\cdot}C_6H_4{\cdot}CH_3(p)$ contains at least two oily members, and the experiments were not further continued in this direction.

The benzyl-derivative of diazoamidobenzene has been prepared by direct benzylation by Friswell and Green (Trans., 1886, 749), who state that it is a solid melting at 81°. We have prepared the corresponding derivative of diazoamidoparatoluene, which, after purification by crystallisation from alcohol with the addition of animal charcoal, forms ochreous needles melting at 114°.

I. 0·1164 gram gave 0·340 gram CO_2 and 0·0704 gram H_2O.
II. 0·1430 „ 15·8 c.c. moist N at 11° C. and 769·5 mm. bar.

	Calculated for $(p)CH_3{\cdot}C_6H_4{\cdot}N_3(C_7H_7){\cdot}C_6H_4{\cdot}CH_3(p)$.	Found. I.	Found. II.
C	80·00	79·66	—
H	6·66	6·71	—
N	13·33	—	13·34

* We are indebted to Dr. A. Weinberg of the Frankfürter Anilinfarben-Fabrik, Gans and Co., for a quantity of this substance prepared in their factory.

These benzyl-derivatives do not decompose under the influence of acids in the same definite manner as do the other alkyl-derivatives when treated in the same way. A large amount of tarry matter and intensely-coloured products, possibly benzylated amidoazo-compounds, are always formed in this decomposition.

9. *The Action of Diazotised Nitranilines on Parachloraniline and of Diazotised Parachloraniline on the Nitranilines.*

In order to ascertain whether a mixed diazoamido-compound containing nitrobenzene and chlorobenzene residues could be obtained, diazotised metanitraniline was allowed to act upon parachloraniline, and diazotised parachloraniline upon metanitraniline in the usual way. A bulky, pale yellowish product was obtained in each case, and this, although apparently a homogeneous substance, was soon found to be a mixture from which metadinitro-diazoamidobenzene (m. p. 194°) was easily separable by fractional crystallisation.

Attempts made with paranitraniline and parachloraniline led to similar results whichever order of mixing was adopted. The product was always a mixture containing paradinitro-diazoamidobenzene (m. p. 223°), and in some preparations free nitraniline was found. In one case, when diazotised paranitraniline had been made to act on parachloraniline in hydrochloric acid solution (no sodium acetate being used), a very small quantity of a substance having the properties of the mixed diazoamido-compound sought for was isolated from the mixture of products. The substance in question appeared mixed up with the needle-shaped crystals deposited from the alcoholic solution of the original preparation, and formed ochreous crystals of great brilliancy consisting of small, well-formed octohedra which, on account of their much greater density, could be easily washed out of the mass of fine needles with which they were entangled. The crystals thus separated had a melting point of 181°, which was not altered by another crystallisation from alcohol; at the instant of fusion, the compound froths up and decomposes. A chlorine determination gave the following results:—

0·1126 gram gave 0·0598 gram AgCl.

	Calculated for $(p)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4Cl(p)$.	Found.
Cl	12·83	13·13

The substance possessed the properties of a mixed diazoamido-compound, dissolving in alcoholic alkali with an intense red colour, and being reprecipitated by acids in a yellow flocculent condition.

The yield of this compound was too small to make it worth while to prepare it in quantity.

The foregoing experiments are of importance in connection with the present investigations, as showing that two dissimilar amines may fail to combine to form a mixed diazoamido-compound, or that the formation of such a compound may take place only to a subordinate extent, the chief products being normal diazoamido-compounds. In other words, there may be a degree of dissimilarity between the two amines which is incompatible with the stability of the mixed diazoamido-compound. In the present imperfect state of our knowledge of the chemical constitution of the diazoamido-compounds, it is of course impossible to follow the precise course of the change which leads to the production of a mixture of normal compounds from a mixed compound, but two explanations naturally suggest themselves. Supposing the unstable mixed compound to be momentarily produced, this might be regarded as decomposing into a mixture of free diazosalts and amines in accordance with known facts :—

$$X{\cdot}N_3H{\cdot}Y \text{ giving}$$

$X{\cdot}N_2{\cdot}OH$	$X{\cdot}NH_2$
$Y{\cdot}N_2{\cdot}OH$	$X{\cdot}NH_2$.

These four products might then be supposed to recombine with the formation of the normal compounds—

$$X{\cdot}N_3H{\cdot}X \text{ and } Y{\cdot}N_3H{\cdot}Y.$$

The alternative explanation is that the mixed compound reacts with itself in accordance with the scheme—

$$2X{\cdot}N_3H{\cdot}Y = X{\cdot}N_3H{\cdot}X + Y{\cdot}N_3H{\cdot}Y.$$

10. *The Action of Diazotised Metanitraniline on Ethylparachloraniline and of Diazotised Parachloraniline on Ethylmetanitraniline.*

Ethylparachloraniline hydrochloride was dissolved in water and the solution of metanitrodiazobenzene chloride added, the mixture being kept well cooled and allowed to stand for about 12 hours. The reddish precipitate was collected and washed, and purified by two or three crystallisations from dilute alcohol with the addition of animal charcoal. The pure substance crystallises in long, flat, lustrous plates of an ochreous colour melting at 106°.

I. 0·1647 gram gave 0·3343 gram CO_2 and 0·0651 gram H_2O.
II. 0·0668 „ 10·85 c.c. moist N at 16·5° and 733·3 mm. bar.
III. 0·2120 „ 0·0999 gram AgCl.

	Calculated for $(m)NO_2{\cdot}C_6H_4{\cdot}N_2(C_2H_5){\cdot}C_6H_4Cl(p)$.	Found. I.	II.	III.
C.....	55·17	55·35	—	—
H.....	4·26	4·39	—	—
N.....	18·39	—	18·15	—
Cl.....	11·65	—	—	11·64

The substance is decomposed by cold hydrochloric acid into metanitrodiazobenzene chloride and ethylparachloraniline.

The isomeric compound was prepared in a precisely similar manner by the action of diazotised parachloraniline on ethylmetanitraniline. After purification by crystallisation from alcohol, with use of animal charcoal, it forms long, flat, pale-yellow needles melting at 129·5°.

I. 0·1172 gram gave 0·2364 gram CO_2 and 0·0458 gram H_2O.
II. 0·1078 „ 0·0521 gram AgCl.

	Calculated for $(p)ClC_6H_4{\cdot}N_2(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$.	Found. I.	II.
C	55·17	55·01	—
H	4·26	4·34	—
Cl.....	11·65	—	11·94

The compound is resolved by cold hydrochloric acid into parachlorodiazobenzene chloride and ethylmetanitraniline.

The pair of isomerides now described are probably members of a triplet of which the third modification is wanting, owing to the circumstance that a mixed diazoamido-compound cannot be prepared from parachloraniline and metanitraniline by the ordinary methods.*

11. *Quantitative Decomposition of Diazoamido-compounds.*

In a previous paper (Trans., 1887, 438), we made known a method for converting the products of decomposition of the diazoamido-compounds by hydrochloric acid into stable compounds, easily separable and capable of identification. This method gave such satisfactory results for the purposes of qualitative identification, that we have been induced to apply it quantitatively, and, as will be seen from the numbers submitted, the process has proved equally serviceable from this point of view. In order to estimate the amount of free diazo-chloride formed by the acid, the process has been modified as follows:—

* It is possible that the desired compound may be obtained by acting with 1 mol. of a solid metanitrodiazobenzene salt on 2 mols. of parachloraniline dissolved in some non-aqueous liquid such as benzene. It is proposed to test this method experimentally.

A weighed quantity of the finely powdered substance is placed in a small beaker, and after being covered with an excess of strong hydrochloric acid, is allowed to stand with occasional stirring till the whole or nearly the whole of the substance is dissolved. The solution is then diluted with a little water and filtered through a tared filter, the residue being washed on the filter, dried, and weighed, and its weight subtracted from that of the substance employed. The filtrate is allowed to fall into an alkaline solution containing an amount of β-naphthol slightly in excess of that required by theory, the precipitate is collected, washed free from excess of alkaline solution, then washed with hydrochloric acid to remove the amine, and finally washed with hot water, dried, and weighed on a tared filter. The weight of azonaphthol-compound is then compared with that required by theory in accordance with the general equations:—

$$X{\cdot}N_3H{\cdot}X + HCl = X{\cdot}N_2{\cdot}Cl + X{\cdot}NH_2,$$
$$X{\cdot}N_2{\cdot}Cl + C_{10}H_7{\cdot}ONa = X{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + NaCl.$$

With some compounds, it was found advantageous to allow the acid filtrate to drop into an acid solution containing the β-naphthol in suspension instead of dissolved in alkali. After being allowed to stand for some hours, the liquid is gradually made alkaline, and the precipitate collected and treated as before. For the sake of brevity, the words "acid" or "alkaline treatment" will be used to indicate the method employed. We now give the numerical results:—

I. Compound produced by the action of diazotised metanitraniline on ethylparachloraniline. M. p. 106°. Alkaline treatment.

0·3580 gram (less 0·0014 gram residue) gave 0·3420 gram azonaphthol-compound = 95·9 per cent. The azonaphthol after crystallisation had a melting point of 194° (metanitrobenzeneazo-β-naphthol). According to theory, 100 parts of the substance should yield 96·5 parts of azonaphthol-compound.

II. Compound produced by the action of diazotised parachloraniline on ethylmetanitraniline. M. p. 129·5°. Alkaline treatment.

0·5076 gram (less 0·002 gram residue) gave 0·4678 gram azonaphthol-compound = 92·5 per cent. According to theory, 100 parts of the substance should yield 92·8 of azonaphthol-compound. The substance required 13 c.c. of strong hydrochloric acid and five hours' digestion before the decomposition was sufficiently complete. The product weighed was purified by crystallisation from alcohol and then formed long needles of a deep orange-red colour; the melting point is 162·5°. Analysis showed the substance to be—

Parachlorobenzeneazo-β-naphthol.

0·2346 gram gave 0·1210 gram AgCl.

	Calculated for $(p)ClC_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$.	Found.
Cl	12·56	12·75

III. Ethyl-derivative of paradichloro-diazoamidobenzene. M. p. 85·5°. Alkaline treatment.

0·5206 = (less 0·0002 gram residue) gave 0·4968 gram azonaphthol-compound = 95·5 per cent. Theory requires 96·1 per cent. The substance required 8 c.c. strong acid, and was decomposed in 15 minutes. The azonaphthol-compound was the same as in the last analysis.

IV. Compound produced by the methylation of metadinitrodiazoamidobenzene. M. p. 127—128°. Alkaline treatment.

0·2378 gram (less 0·0060 gram residue) gave 0·2246 gram azonaphthol-compound = 96·8 per cent. Theory requires 97·3 per cent., 5 c.c. acid used; time required for decomposition, 45 minutes. Azonaphthol-compound identified as metanitrobenzeneazo-β-naphthol (m. p. 194°).

V. Compound produced by the methylation of paranitrodiazoamidobenzene. M. p. 219°. Alkaline treatment.

0·3758 gram (less 0·0076 gram residue) gave 0·3598 gram azonaphthol-compound = 97·7 per cent. Theory requires 97·3 per cent. Substance very difficult to decompose; 15 c.c. strong acid required 24 hours at ordinary temperature; the decomposition had to be completed by heating at 90° for one hour. Azonaphthol-compound identified as paranitrobenzeneazo-β-naphthol (m. p. 250°).

VI. Compound produced by methylation of the mixed diazoamidocompound from meta- and para-nitraniline. M. p. 148°. Alkaline treatment.

0·2816 gram (less 0·0122 gram residue) gave 0·2650 gram azonaphthol-compound = 98·3 per cent. Theory requires 97·3 per cent. Substance decomposes much more easily than the preceding isomeride; 10 c.c. acid produced decomposition in one hour. Azonaphthol-compound a mixture of meta- and para-nitrobenzeneazo-β-naphthol.

VII. Compound produced by the action of diazotised paranitraniline on methylmetanitraniline. M. p. 168°. Alkaline treatment.

0·2658 gram (less 0·0088 gram residue) gave 0·2478 gram azonaphthol-compound = 96·4 per cent. Theory requires 97·3 per cent. 11 c.c. acid required, and three and a half hours at ordinary temperature. Azonaphthol-compound identified as paranitrobenzeneazo-β-naphthol (m. p. 250°).

VIII. Compound produced by the action of diazotised metanitraniline on methylparanitraniline. M. p. 176—177°. Acid treatment.

0·2567 gram (less 0·0156 gram residue) gave 0·2302 gram azonaphthol-compound = 95·4 per cent. Theory requires 97·3 per cent.

12 c.c. acid allowed to act for six hours, then filtered into acid solution containing β-naphthol, and allowed to act for 12 hours, after which the mixture was made alkaline and treated as usual.

This compound is the only one which has given unsatisfactory results by the alkaline method, the percentage of azonaphthol-compound always coming out too high. It is probable that the precipitate retains methylparanitraniline which is imperfectly removed by acid washing, owing to its feeble basic properties. The result obtained by the acid method is nearly 2 per cent. too low, although every precaution was taken to insure accuracy. With this exception, however, the numbers obtained are sufficiently exact to enable us to say that the decomposition of the diazoamido-compounds by cold hydrochloric acid takes place quantitatively in accordance with the general equation—

$$X{\cdot}N_3H{\cdot}X + HCl = X{\cdot}N_2{\cdot}Cl + XNH_3.$$

The value of this method would of course be greatly enhanced if it were possible to ascertain exactly in the case of *mixed* diazoamido-compounds how much of each radicle is set free by the decomposition. Thus the azonaphthol-compound in such a case consists of the mixture—

$$X{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + Y{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

It is only necessary, therefore, to find some method of estimating the amount of X or Y in the azonaphthol-mixture in order to get at the desired result. Experiments in this direction with the mixed compound, $(p)ClC_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}CH_3(p)$, are now in progress.

The triplet of methyl-derivatives of dinitrodiazoamidobenzene described in the present paper furnish another instance towards the generality of the isomerism which is now undergoing investigation. Our chief object in extending these researches will be to secure, if possible, triplets of mixed isomerides free from nitro-groups, and experiments having this end in view have already been commenced.

It gives us great pleasure, in conclusion, to express our thanks to Mr. E. H. R. Salmon, who has given us material assistance by making most of the analyses and by preparing many of the materials used in the course of the investigation.

Finsbury Technical College,
May 10th, 1888.

LII.—*The Optical and Chemical Properties of Caoutchouc.*

By J. H. Gladstone, Ph.D., F.R.S., and Walter Hibbert, F.I.C.

In a paper on Essential Oils, published in the Trans., 1886, 609, one of us gave some observations on the refraction and dispersion of caoutchouc, as well as on isoprene and caoutchene derived from it by distillation. As these seemed to show that the caoutchouc is a hydrocarbon in which at least two pairs of carbon-atoms are doubly linked, it was deemed interesting to pursue the inquiry further.

We have met with great difficulties, partly from the doubtful purity of the substance, partly from the readiness with which it undergoes transmutations. We think, however, that some of the results arrived at may not be without value.

The earlier workers on the subject were able to get the natural juice of the tree, but the analyses, including those of Faraday and Greville Williams, indicate the presence of some impurities. At the present day, the juice is no longer imported. The substance we used was the best Para rubber, kindly placed at our disposal by Mr. Willoughby Smith, as well as another specimen of it, and of Penang rubber obtained from Mr. Hancock.

Para Rubber.

This rubber was pale in colour, in pretty uniform laminæ, and had a sp. gr. of about 0·92. On analysis, it contained, as might have been expected from its origin, some inorganic constituents. In Willoughby Smith's specimen, this was found to be 0·46 per cent., and in Hancock's 0·38 per cent. Another constituent was water, and to an extent that was not expected by us. Willoughby Smith's specimen gave 10·6 and 11 per cent., Hancock's 7·1. As this water came off at 100°, it probably indicates nothing but insufficient drying.

It is well known that part of the caoutchouc is soluble in benzene and other solvents, and that a part is insoluble. Faraday also speaks of albumin as one of the constituents of the juice. We found the best solvent to be chloroform. This very slowly dissolves the whole of the hydrocarbon, leaving a sort of network of the nitrogenous body. In one experiment, this residue was found to be about 4 per cent. of the whole weight. We are inclined to believe that the less soluble modification of the hydrocarbon which has been frequently observed, is produced during the drying of the juice, for we find that if the more soluble part be heated, it is more or less changed, and less susceptible of subsequent solution. The change increases as the

temperature is raised, and also with the length of time during which the heat continues. This will account for the very varied results obtained by different experimenters as to the proportions of soluble and insoluble caoutchouc.

We made many attempts to separate these two modifications, and to remove the oxidised product which commonly occurs with them. The most promising method seemed to be to dissolve the rubber in cold chloroform, and precipitate partially with a little alcohol. The precipitate obtained was generally dried in a vacuum, in order to avoid oxidation. We failed, however, to produce any good separation, and the results of analyses gave usually about 3 per cent. of oxygen, nor was this oxygen removed by the action of sodium on the solution. One small specimen, however, gave the following numbers, which closely approach those deduced from $C_{10}H_{16}$:—

0·1164 gram gave 0·3733 CO_2 and 0·1258 H_2O.

	Found.	Calculated.
Carbon.....	87·46	88·24
Hydrogen	12·00	11·76
	99·46	100·00

Optical Analysis.

Accepting it as a fact, that the carbon and hydrogen in the principal constituent of caoutchouc are in the same proportions as in the essential oils, there remains the question as to the arrangement of the elements. It is quite easy to conceive that the $C_{10}H_{16}$ is so built up that only one pair of carbon-atoms is double linked as in the terpenes, or two pairs as in the citrenes, or there may be three pairs. Nor does it follow that $C_{10}H_{16}$ is its molecular formula: C_5H_8 exists as one of its distillation products, and $C_{15}H_{24}$ is not uncommon among essential oils. Now a knowledge of the refraction and dispersion of the substance would probably determine the first question, and might throw light on the second.

The theoretical refraction and dispersion equivalents of $C_{10}H_{16}$ in the three conditions above mentioned, would be as follows, assuming that each pair of doubly-linked carbon-atoms would produce the same increment as in the aromatic series.

$C_{10}H_{16}$.	$P\frac{\mu_A - 1}{d}$.	$P\frac{\mu_H - \mu_A}{d}$.
1 pair of doubly-linked carbons ..	73·0	4·0
2 " " " ..	75·2	4·8
3 " " " ..	77·4	5·6

In order to determine this point, a number of specimens prepared in various ways were dissolved in benzene, and the optical determinations made as usual. The following are the whole of the results obtained, with the exception of three which were known to be untrustworthy.

TABLE I.

No. of preparation.	Strength of solution.	Refraction equivalent.	Dispersion equivalent.
1	16·44	76·02	5·13
2	16·66	76·90	4·90
3	13·27	74·20	5·02
4	19·71	73·42	5·31
5	11·44	73·23	4·87
6	30·40	74·58	5·01
7	5·83	75·11	5·60
8	14·14	76·94	5·01
9	12·83	75·69	5·19
10	18·24	76·87	5·67
11	17·58	77·59	5·34
12	8·24	75·43	5·44
13	15·38	75·69	5·40
14	10·32	74·46	6·13
15	12·18	76·02	5·69
16	9·42	76·52	5·63
17	13·92	76·01	5·18

Nos. 1 and 2 were made from the original rubber as dissolved in chloroform and dried at 100°. The others, from 3 to 13, were made from the substance that was precipitated by alcohol from the chloroform solution. This precipitate was dried in different ways: No. 3 at 100° in hydrogen gas; No. 4 in a Sprengel vacuum at 40°; No. 5 over sulphuric acid for seven days; Nos. 6, 7, 8, were parts of the same preparation of which the carbon and hydrogen constituted 97·2 per cent. No. 8 was No. 7 concentrated by evaporation. No. 10 and 11 are alluded to below. No. 13 was dried in hydrogen at 100°. Nos. 14 and 15 were the first and second fractions of a precipitate obtained by adding alcohol to an ethereal solution of the original Para rubber. Nos. 16 and 17 were respectively the first and second precipitates similarly obtained from an ethereal solution of Penang rubber. It will be observed that there is no well-marked difference between these first and second precipitates.

Now, although the refraction and dispersion equivalents in the above table vary more than is easily accounted for, they all agree in showing that the $C_{10}H_{16}$ must have more than one pair of carbon-atoms doubly linked. All the dispersion equivalents and 11 of the

refraction equivalents, also exceed what theory requires for two pairs of carbon-atoms so combined. They fall short of what would be required by three pairs, at any rate in the case of refraction, but it must be remembered that the presence of a little oxygen in the substances examined will pull down the refraction and dispersion considerably. 3 per cent. of oxygen for instance would make a reduction of at least 1·4 in the refraction column and 0·13 in the dispersion column, and if the addition of oxygen caused some of the carbon to be saturated, the reduction would be still greater. It is worthy of remark that the lowest figures are in No. 5, where there was a long exposure to air during drying.

The best observations are Nos. 10 and 11. For these, the chloroform solution was very carefully mixed with alcohol, which caused the caoutchouc as it separated to rise to the surface like cream. After separating, this cream was heated in hydrogen at 140°, and afterwards dried in a Sprengel vacuum at 125°. In this way, we succeeded in preparing a substance of which the hydrocarbon formed 99·46 per cent. The analysis has already been given. The solution was made in the case of No. 10 by dissolving a known weight of this caoutchouc in a known weight of benzene. In the case of No. 11, the strength of the solution was determined by subsequent evaporation. The observations show a heightening of both optical properties, in fact, the mean refraction equivalent 77·23 and dispersion equivalent 5·50 almost coincide with the calculated figures 77·4 and 5·6 given above.

We have little doubt, therefore, that the main constituent of caoutchouc is a compound which for $C_{10}H_{16}$ has three pair of carbon-atoms doubly linked.

If this be the case, the molecular formula cannot be C_5H_8, like isoprene, or $C_{15}H_{24}$, like cedrene, as these would give respectively one and a half and four and a half pairs of carbon-atoms united by double linking. It cannot contain the hexagonal ring, but must be expressed graphically by a chain formula. This may account for the wide difference of properties between caoutchouc and the various essential oils.

Halogen Compounds.

An endeavour was made to test the previous conclusions by chemical methods. The chloroform solution appeared to offer a good opportunity of studying the action of halogens on caoutchouc, and the results were, considering the small amount of oxygen always present, sufficiently definite.

We did not succeed in obtaining a simple additive compound with chlorine. On passing the gas into a chloroform solution of caoutchouc containing about 1 per cent. of the hydrocarbon—the experiment being

made in weak diffused light—fumes of hydrochloric acid were at once evolved, and this continued for a very long time. The general results of many experiments indicate that substitution and addition were taking place simultaneously. On evaporating the solution, a residue was always obtained in slightly yellow scales. Different specimens did not give the same results on analysis. The best preparation which we succeeded in making gave the following figures :—

0·0575 gram gave by Carius' method 0·1515 AgCl.
0·1067 „ 0·1108 CO_2 and 0·0305 H_2O.

Carbon	28·32
Hydrogen	3·17
Chlorine	65·18
	96·67

The presence of oxygen renders the true interpretation of these figures somewhat uncertain, but they agree fairly with the ratio $C_{10}H_{14}Cl_8$, which will require for 28·32 per cent. of carbon, 3·3 per cent. hydrogen and 66·95 per cent. chlorine. Such a result is in accordance with the view that the hydrocarbon contains six unsaturated atoms of carbon, and is not easily explained on any other supposition.

Action of Bromine.—Bromine acts energetically on caoutchouc dissolved in chloroform, fumes of hydrobromic acid being evolved. But a weak solution of bromine in chloroform, while acting at once, does not give rise in the first instance to a very rapid separation of hydrobromic acid, though upon standing, the gas slowly appears. This suggested the making of a synthetic and volumetric determination of the proportions in which caoutchouc and bromine combine. Standard solutions of each were therefore prepared, and the latter was added from a burette to a measured quantity of the former. As the close of the experiment was approached, the bromine disappeared a little less quickly. The flask containing the liquid was then shaken, and a drop taken out by means of a glass rod was brought into contact with a drop of potassium iodide starch solution. When the blue iodide of starch appeared, the presence of free bromine was shown, and this was taken to indicate the completion of direct combination between the bromine and caoutchouc.

The following are the figures obtained :—

The solution of bromine contained 0·03609 gram per c.c.
The solution of caoutchouc contained 0·02458 gram per c.c.

TABLE II.

Caoutchouc taken.	Bromine used.	Bromine used, calculated for 136 parts of caoutchouc.
0·1229 gram	0·2670 gram	295·5
0·1229 „	0·2634 „	291·5
0·4917 „	1·0570 „	292·4
	Mean..	293·1

This number (293) was judged to be somewhat too low, since the very faintest indication of free bromine had been accepted as an indication of completed action. A better and quicker method of determining the value was founded on the subsequent observation that iodine did not act on the solution of caoutchouc in chloroform. It occurred to us that by first adding an excess of bromine, and then a strong solution of potassium iodide, we should get a quantity of iodine set free equivalent to the excess of bromine, and the free iodine could be estimated at leisure by thiosulphate.

On trial of this method, very fairly accordant results were obtained:—

The solution of bromine contained 0·03684 gram per c.c.
The solution of caoutchouc contained 0·0281 gram per c.c.

TABLE III.

Caoutchouc taken.	Bromine added.	Excess of bromine.	Bromine required.	Bromine required for 136 parts caoutchouc.
gram.	gram.			
0·141	0·3684	0·05157	0·3168	305·5
0·141	0·3684	0·05268	0·3157	304·5
0·141	0·3684	0·05157	0·3168	305·6
0·1692	0·4420	0·0663	0·3757	302·6
0·1692	0·4052	0·0405	0·3647	293·1
0·141	0·3352	0·0221	0·3131	301·9
0·141	0·3205	0·0051	0·3151	303·9
0·141	0·3168	0·00368	0·3131	301·9
0·282	0·6447	0·0173	0·6274	302·5
0·141	0·3278	0·0081	0·3197	308·3

The average result is that 136 grams of caoutchouc combine with 303 grams of bromine.* Supposing that 1 mol. of $C_{10}H_{16}$ combined

* Greville Williams has employed bromine to test the saturating power of caoutchene, one of the hydrocarbons obtained by the destructive distillation of caoutchouc. The properties of caoutchene allowed a simpler procedure to be followed. His experiments show that 136 grams of caoutchene combine with 315 grams of bromine.

directly with 4 atoms of bromine to form the tetrabromide $C_{10}H_{16}Br_4$, it would require 320 grams of bromine. When we consider that the caoutchouc experimented on contained about 3 per cent. of oxygen, the figures obtained appear as satisfactory as could be expected. The result does not agree of course with the constitution assigned above to caoutchouc, and can be reconciled only on the supposition either that the action of the halogen has produced an isomeric change, or that the tetrabromide formed is not yet a saturated compound.

Attempts were made to isolate this compound by evaporating down the solution, or by precipitating with a large excess of ether. The precipitate was a white, solid body, but it always proved to be unstable on drying, with loss of hydrobromic acid.

Prolonged Action of Bromine.—A fair excess of a solution of bromine in chloroform was added to a solution of caoutchouc in chloroform, and allowed to act at ordinary temperatures for three days. Fumes of hydrobromic acid were evolved all the time. The solution was then poured into a considerable quantity of ether, which caused a white precipitate. This was separated by filtration and washed with ether. When dried at 60°, it was quite white, and easily powdered.

0·1312 gram gave 0·1091 CO_2 and 0·0348 H_2O.
0·1226 „ 0·2095 AgBr
0·1054 „ 0·1819 „
0·1270 „ 0·2182 „
} Estimated by Carius' method.

	Found.				Calculated for
	I.	II.	III.	IV.	$C_{10}H_{15}Br_5$.
Carbon.....	22·67	—	—	—	22·43
Hydrogen....	2·94	—	—	—	2·80
Bromine.....	—	72·71	73·43	73·10	74·76

Remembering that some oxygen was present, the experimental results agree sufficiently well with those calculated from the formula $C_{10}H_{15}Br_5$. It seems not improbable that this body is formed from a compound, $C_{10}H_{16}Br_6$, by the elimination of HBr.

Iodine.—We have already stated that iodine has little or no action on caoutchouc dissolved in chloroform. It is, perhaps, worthy of note that Adriani (*Chem. News*, **2**, 278) says that the action of iodine on the globules in the natural juice is more marked than that of bromine.

Action of Heat.

The ordinary statement is that caoutchouc, when heated, softens and melts at about 200°; that if cooled again it never becomes hard as before.

We found that the fusing point depended partly upon the exposure of the substance to air, oxidation affecting the result. 0·5 gram of caoutchouc was heated at 200° for two hours in a sealed tube filled with hydrogen. There was only a slight superficial fusion, and scarcely any decomposition.

A solution of caoutchouc in toluene was also heated in a sealed tube at 200° for two hours, and the solvent then distilled off at 112° in a Sprengel vacuum. It left a hard residue, and there was no odour of decomposition. Even when heated at 210° in a Sprengel vacuum, caoutchouc was found to be only superficially melted, though after that treatment it dissolved very slowly in benzene.

In order to ascertain whether the optical properties of caoutchouc were changed by heating, we dissolved some of Hancock's Para rubber in toluene, determined its refraction and dispersion, then exposed the solution in a sealed tube to a temperature of 200° for three hours, and after cooling, examined it afresh. The solution was found far more limpid than it had previously been. The other properties were as follow. The solution contained 12·85 per cent. of caoutchouc:—

	Temperature.	Sp. gr.	μ_A.	μ_H.
Before heating ..	19·4°	0·8706	1·4896	1·5295
After „ ..	18·5	0·8708	1·4895	1·5294

These figures are practically identical, and it may be concluded that if the heating has produced any change, it has not affected the proportion of carbon-atoms doubly linked. It is evident also that its molecular volume in solution has not been affected.

The optical properties of the caoutchouc as deduced from the above figures are: refraction equivalent, 76·46; dispersion equivalent 5·40, which confirm the observations made from the solutions in benzene.

When caoutchouc is heated considerably above 200°, it is converted into a mixture of liquid oils which are believed to be isomeric or polymeric with the original substance. From the distillate have been separated and more or less fully described, isoprene, caoutchene, and heveene.

Isoprene, C_5H_8, has been already shown to contain two pairs of doubly-linked carbon-atoms (Trans., 1886, 619).

Caoutchene, $C_{10}H_{16}$, was shown at the same time to have two pairs of doubly-linked carbon-atoms. The ratio of unsaturated carbon to molecular weight is here only half that of isoprene.

We prepared two specimens of caoutchene by repeated fractional distillation; the first from a quantity of oil made by ourselves from Para caoutchouc, the other from oil obtained from Messrs. Hopkin and Williams. The examination of these gave the figures shown in

Tables IV and V, Nos. 1 and 2. The second specimen, when distilled from sodium several times, gave the figures of No. 3, showing that it was practically unchanged, notwithstanding the appearance of a little red flocculent matter.

Heveene.—From the same two mixtures, we also separated a liquid boiling at about 315°. It was dark in colour and became darker on standing. The results of observation are given in Nos. 4 and 5, and are very accordant.

The product boiling above 320° was still darker in colour. The observations made upon it are given in No. 7. The sp. gr. is increased, but the specific optical properties remain practically the same as those of heveene.

As the refraction equivalent in these cases was a little lower than we should have expected on the supposition that these bodies of higher boiling point were similar in composition to caoutchouc, we thought they might contain some quantity of an oxygen product. On treating our heveene with sodium, we found that some hydrogen was liberated, and it was therefore redistilled from sodium several times. A nearly colourless oil was obtained having an intense blue fluorescence. This caused the spectrum to be nearly cut off between G and H. The results of observation are given in No. 6, showing that it has been only slightly increased in refraction and dispersion. Several attempts to obtain the vapour-density failed, apparently through some molecular change taking place in the vapour itself when highly heated.

TABLE IV.

No.	Substance.	Boiling point.	Temp.	Sp. gr.	Refractive index.		
					A.	F.	H.
1	Caoutchene.....	174—176°	18·0°	0·8377	1·4657	1·4807	1·4950
2	„	173—177	19·0	0·8361	1·4644	1·4791	1·4938
3	„	173—178	22·0	0·8350	1·4638	1·4793	1·4939
4	Heveene	300—320	17·8	0·9146	1·5009	1·5172	—
5	„	310—316	16·5	0·9291	1·5090	1·5265	—
6	„	312—318	22·6	0·9245	1·5074	1·5249	1·5421
7	Higher product ..	above 320	16·3	0·9487	1·5190	1·5371	—

After distilling off the highest product there remained a quantity of a substance not volatile at low redness, and which on cooling became quite hard. As the whole had been originally distilled, we may suppose that this product had been formed by the subsequent action of heat; indeed there were other indications that polymerisa-

TABLE V.

No.	Substance.	Refraction equivalent.	Dispersion equivalent.	
			F – A.	H – A.
1	Caoutchene	75·60	2·44	4·76
2	„	75·54	2·39	4·78
3	„	75·54	2·53	4·90
4	Heveene	74·48	2·43	—
5	„	74·51	2·56	—
6	„	74·64	2·58	5·11
7	Higher product	74·40	2·60	—

tion took place during redistillation. It is probable also that there are bodies produced which are intermediate in boiling point between those examined.

The general results of the destructive action of heat upon caoutchouc may therefore be considered as involving no change in the proportion of carbon to hydrogen, but changes of structure in the hydrocarbon which are best represented by the following optical constitutional formulæ. In this table, C″ is used for carbon having the refraction equivalent 6·1 and dispersion equivalent 0·66.

Substance.	Optical constitutional formulæ.
Caoutchouc	$n\mathrm{C''_5C_4H_{16}}$
Isoprene	$\mathrm{C''_4CH_8}$
Caoutchene	$\mathrm{C''_4C_6H_{16}}$
Heveene	$n\mathrm{C''_2C_3H_8}$.

Since the paper was read at the Society's meeting, we have endeavoured to determine the molecular weights of caoutchouc and heveene by Raoult's method.

For heveene, we obtained depressions of 1·85° C. and 1·52° C. with solutions containing respectively 9·37 and 7·68 grams to 100 of benzene. These figures give 248 and 247·5 for the molecular weight of heveene, which strongly indicates the formula $\mathrm{C_{20}H_{32}}$.

As to caoutchouc, the depression obtained with a solution containing 9 parts to 100 of benzene was so very small that its molecular weight must be at least 50 times that of heveene, if the method holds good.

LIII.—*On an Apparatus for Maintaining a Constant Pressure when Distilling under Reduced Pressure.*

By W. H. Perkin, Ph.D., F.R.S.

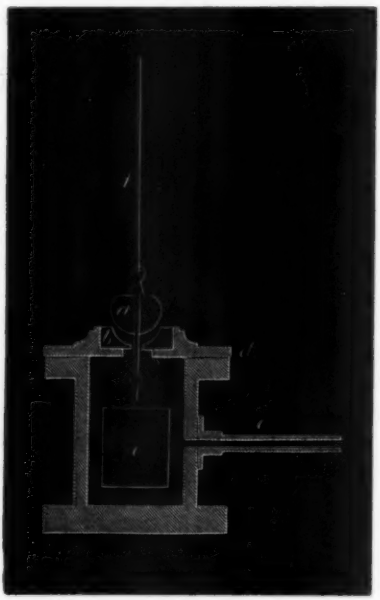
The great value of conducting distillations under reduced pressure in the separation of volatile products from non-volatile ones, in fractioning substances decomposable at high temperatures, &c., is now so well recognised that it is unnecessary to comment upon it, and as it is a method of working so much resorted to at the present time, anything that can render it more simple and manageable is of service. Those who have conducted distillation under reduced pressure know that the constant watching which is usually required to keep the pressure uniform, very much interrupts the attention which it is necessary to give to the distillation itself, and as the work I am engaged in frequently requires me to resort to distillations of this kind, a variety of experiments have been made to obtain some simple and effective automatic arrangement for this purpose, and, thinking the results might be useful to others, I have ventured to lay them before the Society.

The first idea which naturally suggested itself was to regulate the pressure by means of a column of mercury so arranged that air would be drawn through it as soon as the desired reduction of pressure was attained. Arrangements on this principle have been used by Lothar Meyer and others (*Annalen*, **165**, 303; **198**, 218), but my experiments in this direction, especially for large reductions of pressure, were not satisfactory, and some more mechanical method was sought for. The use of a valve opening inwards, and regulated by a lever and weight, was next tried. This, however, was also found to work unsatisfactorily, because when the regulating point was reached a state of equilibrium existed, and directly the air commenced entering vibration set in, the valve chattering, and not coming to rest again until a considerable change of pressure had taken place. This showed that what was wanted was a valve that would act not only with considerable force and decision, both as to opening and closing when the desired reduction of pressure was obtained, but also with very small variations of pressure. This was attained eventually by means of a valve weighted to make it close quickly, and capable of being opened by an electromagnet, the action of the latter being influenced by a column of mercury making electrical contact with a platinum wire as soon as it reached the desired height. An apparatus made on this principle has been in use in my laboratory for several

years, and worked satisfactorily. The following is an account of it given in detail, as there are several points which require attention to make it work well. The description of the apparatus will be understood more easily by reference to the diagrams which are given.

The first thing to be considered is the regulating valve. At first, valves of metal and also of caoutchouc were experimented with, but as they did not work very well, glass was eventually used. The shape of the valve is that of part of a sphere, *a* (Fig. 1), half an inch in diameter; it fits into a glass seating, *b*, to correspond, both surfaces

FIG. 1.



being very carefully ground and polished together; there is a hole passing through the seating for the inlet of air. The valve has a hole drilled through it, into which a wire with hooks on both ends is cemented. One hook is to carry a weight, *c*, the other to suspend the valve to an electromagnet. The valve and seating is fixed into the movable top of a brass cylinder, *d*, in which the weight attached to the valve hangs. A tube, *e*, is inserted into the side of the cylinder to connect it with the part of the apparatus which is to be exhausted by the water-pump or other means. The upper hook on the valve is attached by means of a copper wire, *f*, to a ball and socket joint provided with a long screw passing through the armature of the

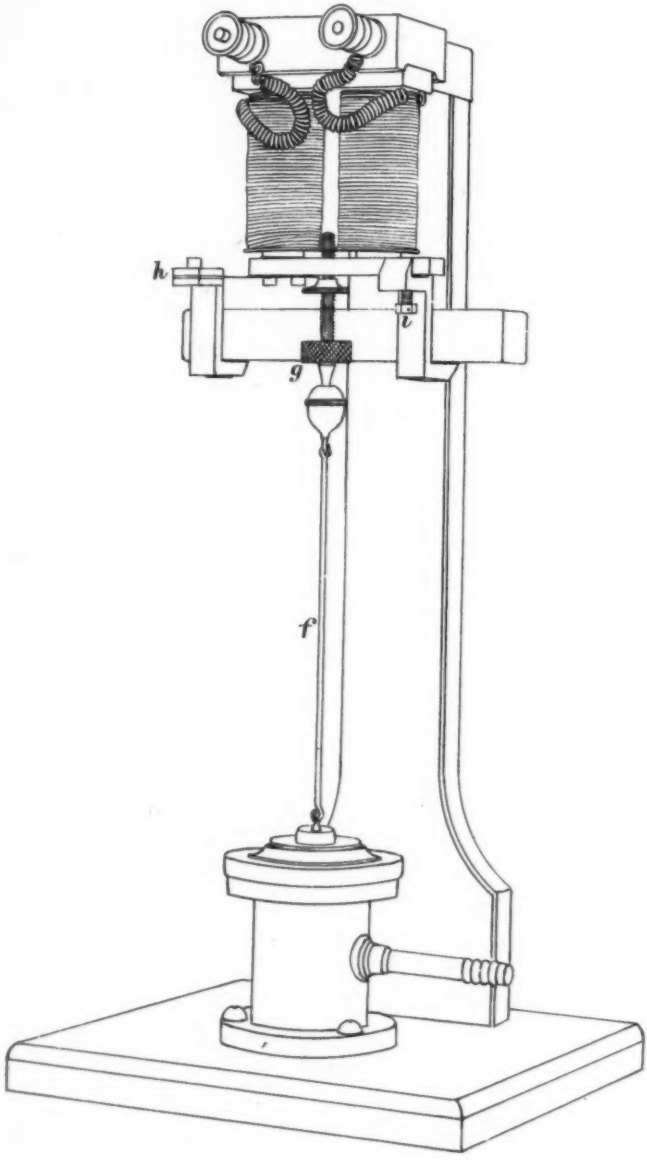


Fig. 2.

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Journ. Chem. Soc. Aug 1888. W. H. PERKIN.

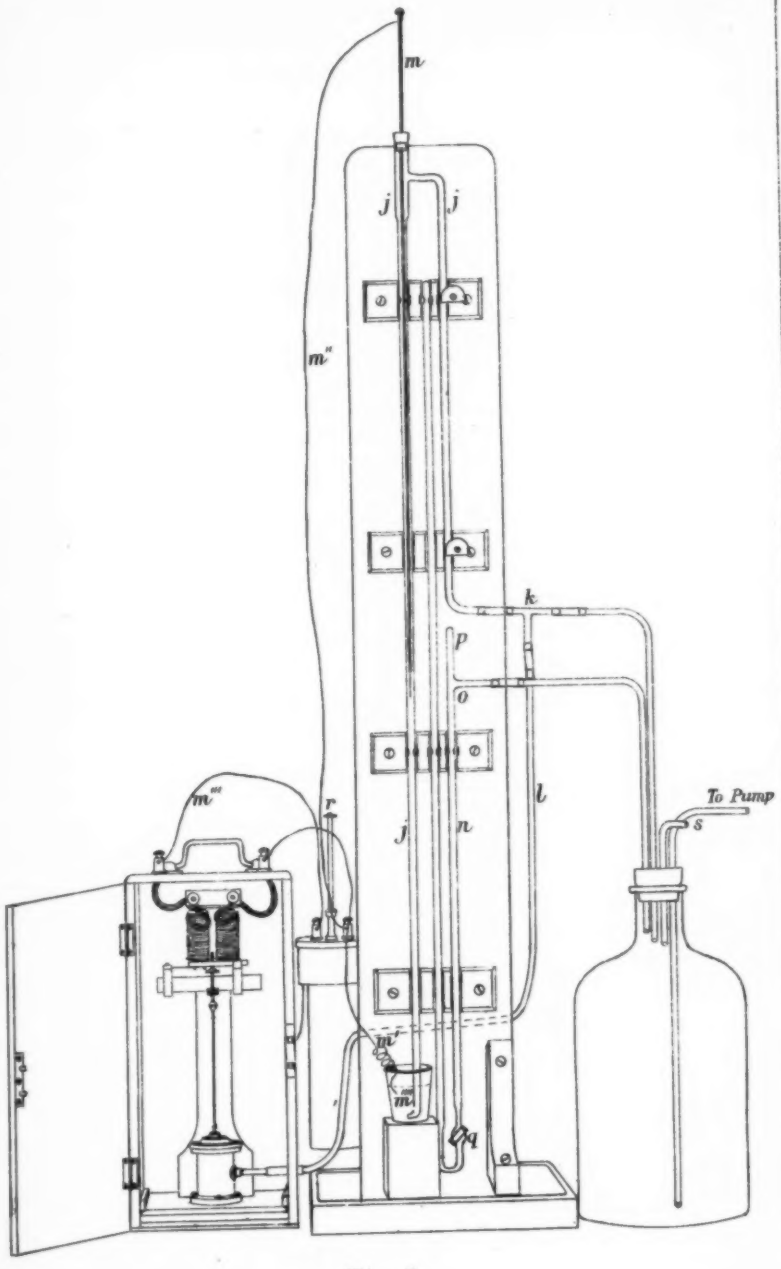

Fig. 3.

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magnet, as seen in Fig. 2; this screw is provided with a milled head, *g*, so that the valve may be adjusted in relation to the armature. There is also a nut above this, and working on this screw, which when tightened up to the armature locks the screw so that the adjustment may not alter by vibration. The electromagnet and other parts of the apparatus are fixed on a *rigid* mahogany stand, as seen in the diagram, and need no explanation. The armature is kept in its place at one end by a steel spring, *h*, the other resting in a brass support provided with an adjusting screw, *i*, so that the distance of the armature from the electromagnet may be arranged when necessary. This apparatus is kept in a box, so that it may not suffer from dust and laboratory fumes, a hole being pierced in the side of the box to receive the connecting tube, whilst binding screws are fastened on its top to connect with the necessary wires.

The arrangement by which the desired reduction of pressure can be regulated consists of a graduated glass tube, about 7 or 8 mm. in diameter, and about 800 mm. long. A piece of tube, about 70 mm. long and 12 in diameter, is fused on to the top, and from its side an ordinary piece of quill tubing passes, being afterwards bent twice at right angles (*j*, *j*, *j*, Fig. 3). This is connected with a T-piece, *k*, one arm of which passes to the receiver, consisting of a strong bottle of about 4 or 5 litres capacity, the other arm being connected with the regulating valve by the tube *l*. A stout copper wire, *m*, about 600 mm. long, passes down the graduated tube; this is provided with a platinum point screwed into it at the lower end, and a binding screw on the upper end. Near the lower end, a piece of copper is screwed on with three projecting points, so as to keep the copper wire in a central position in the tube, *j*. This wire fits air-tight into the enlarged upper part of the tube by means of a vulcanised cork. The lower end of the graduated tube is drawn off sideways, as in Fig. 4, leaving an aperture of about 0·5 mm. diameter (the object of this will be described further on), and is placed in a vessel of mercury, *m''''*, Fig. 3. A thin copper wire, *m'*, passes from the mercury in this vessel to one of the binding screws of the regulating valve. Another, *m''*, passes from the binding screw on the thick copper wire to the battery, and a third, *m'''*, from the second binding screw of the battery to the second one on the regulating valve.

The working of the apparatus will now be easily seen. The copper wire *m* is drawn up till its point corresponds pretty nearly to the height of the column of mercury necessary to be used for the desired pressure. On setting the water-pump in action, the air being gradually removed from the glass bottle, the mercury will rise in the graduated tube *j*, but the moment it touches the platinum point the circuit is completed, and the electromagnet lifts the glass valve so that some

air enters; this causes the mercury column to fall, but the moment it does so the circuit is broken, and the valve closes. It then rises

FIG. 4.

again; the circuit is again completed, and the valve opens, and so on. In this way, when all the adjustments referred to further on are attended to, a nearly perfectly regular pressure may be obtained not varying more than a fraction of a millimetre.

When first trying this apparatus, the graduated glass tube, *j*, *j*, *j*, was not contracted at the bottom, but it was found that owing to the sparking which takes place when contact is made between the wire and the mercury, thus heating the rarefied air in its vicinity, and the action taking place at nearly equal intervals, oscillations were set up in the mercury column, and the apparatus therefore worked unsteadily, but by contracting the end of the tube sufficiently, as in Fig. 4, the oscillations are almost prevented, and the fluctuations of the columns which take place are only sufficient to regulate the pressure, that is, provided the regulating valve be properly adjusted, because it is evident that if it opens too wide it will let in so much air that the mercury will fall some distance before it closes again, and if it does not open sufficiently there will not be enough air admitted to counteract the excess of pumping power of the water-pump; but with a little attention this matter can be arranged by turning the milled head, *g*, Fig. 2, on the regulating valve, so that the quantity of air admitted only slightly influences the column of mercury. When reading the height of the column of mercury in the graduated tube, *j*, *j*, *j*, the depression of the mercury in the reservoir m'''' must not be forgotten to be taken into account.

As the column of mercury in the graduated tube cannot obviously be kept quite quiet, a second tube was originally placed at its side

standing with its open end in the mercury reservoir, the other end being connected with the exhausted receiver, and this was used as a barometer to measure the pressure, and when the apparatus was working well no appreciable fluctuations were noticed in this tube; when measuring the pressure in this way, however, it was always necessary to compare it with an ordinary barometer giving the atmospheric pressure, and subtract the one from the other to get the pressure the apparatus was working at. It was therefore thought that it would be more simple to connect it with a barometer direct instead of using this second tube, and thus get the correct pressure at once. The most convenient way of doing this is by means of a syphon barometer (*n*, Fig. 3), with the return tube made more than long enough to pass the zero point of the graduation. To the side of this, and near its end, a tube, *o*, is fused to connect it with the glass bottle used for the exhausted receiver, the open end of the tube *p* being closed with a cork. To make the apparatus more easy to move about, the syphon barometer is provided with a glass stop-cock, *q*, in the lower part of the return tube, so that by tilting it fills with mercury; the stop-cock being then closed it can be carried about without danger.* When first trying this barometer, it was found to work very unsteadily. Owing to the vacuum in it, it was found to be excessively sensitive to minute changes of pressure, especially when occurring at regular intervals, oscillations setting in, but it was eventually found that by turning the stop-cock, *q*, partially off, taking care not to prevent the action of the barometer, these oscillations practically were stopped; or the same thing can be effected by drawing out the tube which connects the barometer with the exhausted receiver to a fine point; when well adjusted, only slight fluctuations will be seen on the meniscus of the mercury.

This apparatus works successfully at a pressure of 60 mm., this being about the limit of the water-pump with which it has been used, but no doubt it would do equally well for lower pressures. For most work, a pressure of 200—210 mm. is most convenient, as the boiling is then generally pretty steady, and there is no need to make arrangements for the admission of minute quantities of air as when using very low pressures. This pressure gives a reduction of over 40° in the boiling point.

The apparatus employed in conducting the distillations is practically the same as that described by my late assistant Dr. L. T. Thorne (Trans., 1883, 301). It has been in use in my laboratory ever since it was first devised, and is found to be extremely convenient, especially for fractional distillations. It is attached to the tube *s*.

* This would probably be a convenient adjunct to ordinary syphon barometers.

The battery power used for the regulating valve apparatus should only be sufficient to cause the apparatus to work with decision, otherwise if strong sparking takes place between the mercury and the platinum point the surface of the mercury becomes dirty, and the apparatus does not work well; but if the power be kept down, this takes place but slowly if the tube is of the diameter given above. A bichromate battery, as shown at *r*, is convenient, the power being regulated by the distance the zinc is allowed to go into the chromic mixture. The tube, *j*, *j*, *j*, in which this sparking occurs should be attached to the stand in such a way that it can be easily removed for cleaning when necessary. Experiments were made with floats covered with platinum foil so that there should be no sparking on the mercury. It was found that the best floats to work in a tube were small flat discs of metal covered with platinum, upright ones attach themselves to the side of the tube. These work pretty well, but not so sharply as the mercury itself, a certain amount of pressure being sometimes necessary to make good contact, and this necessitates a greater rise in the mercury than is necessary with mercury only, the fluctuation, however, is but small; nevertheless I prefer to use the mercury alone, and to clean the tube when necessary.

The use of a good sized bottle for the exhausted receiver (about 4½ litres) is advantageous, as it assists in keeping the pressure equal and prevents any considerable alteration in it when changing receivers as in fractional distillation, the small amount of air which enters having but little influence.

If using this apparatus in connection with any powerful arrangement for pumping out the air, it would be necessary to restrict the connection with it by means of a stop-cock capable of pretty fine adjustment, or by a tube of fine bore, because it is evident that if the pumping power is in excess of the capability of the valve to let in air, it can no longer act as a regulator. The use of the weight on the valve is not necessary when large reductions of pressure are being maintained, as the atmospheric pressure is sufficient to close it, but for small reductions it is believed to be of service.

Since devising this apparatus my attention has been drawn to a very ingenious pressure regulator devised by F. D. Brown (*Proc. Phys. Soc. Lond.*, 1879, **3**, 68), which has some points in common with mine, but it has the disadvantage of requiring motive power to work it, as well as a battery.

LIV.—*Chlorofumaric and Chloromaleic Acids and the Magnetic Rotatory Power of some of their Derivatives.*

By W. H. Perkin, Ph.D., F.R.S.

In a paper published in the Journal of this Society by the late B. F. Duppa and myself in 1861 (*J. Chem. Soc.*, **13**, 9), an account is given of some experiments upon the "Action of Pentachloride of Phosphorus on Tartaric Acid." The results of these mainly consisted in the formation of a chloride which with water yielded an acid, and to the latter we gave the provisional name of chloromaleic acid for reasons given in the paper. Later on it was shown that this acid yielded succinic acid when treated with nascent hydrogen (*J. Chem. Soc.*, 1863, **16**, 198). Being desirous of examining the magnetic rotatory power of the derivatives of this chlorinated acid, and of getting further chemical information in connection with it, fresh experiments were made, and the following results obtained.

Tartaric and Racemic Acids with Pentachloride of Phosphorus.

About 225 grams of phosphorus pentachloride and 38 grams of finely-powdered tartaric acid were mixed, and heated on the water-bath in a large Wurtz flask until the mixture became liquid. On examining this with the polariscope, it was found to have a permanent rotation of 7′ 6″ for a length of 102 mm. It was distilled until the temperature of the vapour rose to 130°, and then transferred to a smaller retort and again distilled until the temperature of the vapour was 160°, so as to remove as much oxychloride of phosphorus as possible. Finally, the residue was fractioned under reduced pressure (210 mm.), when nearly all distilled over at 142°, a little at last coming over somewhat higher, leaving a small carbonised residue in the retort.

In a second experiment, 280 grams of phosphorus pentachloride were used to 38 grams of tartaric acid; this was a considerable excess of the former, and after the reaction had been completed on the water-bath, and the fluid allowed to cool, part of it crystallised out. The liquid had a smaller permanent rotation than that from the previous experiment, amounting to only 1′ for a column of 102 mm. It was treated as in the previous experiment, and gave a product boiling at about 144° at 210 mm. The yield obtained was about half that required by theory. It had a very small permanent rotation.

Several similar preparations were made with racemic acid dried at 100°. The reaction appears to go more neatly with this acid and the

product obtained is of better quality. It boiled at 141—143°, at 210 mm., a little fluid of higher boiling point coming over at last, leaving a small quantity of carbonised residue. The yield was nearly the same as the weight of racemic acid used.

This substance, as will be seen further on, is chlorofumaric chloride and not chloromaleic chloride. It is a very slightly yellowish liquid boiling at 142—144° corr. under 210 mm., but at 184·5—187·5° corr. under 760 mm. with slight decomposition, the distillate being yellow, the colour becoming darker towards the end of the operation, and the thermometer rising to 195°, hydrogen chloride also being given off and slight carbonisation taking place. When cooled with ice and hydrochloric acid, it does not solidify. It fumes slightly in the air, and when added to water sinks as a heavy oil which gradually dissolves on agitation, leaving any neutral chlorinated oil it may contain. The chloride prepared from tartaric acid usually contains a small quantity of a neutral chlorinated oil, attacking the eyes very much; that prepared from racemic acid was free or nearly so from this product. This oil boils at about 180°, it was not obtained in sufficient quantity for examination. If some quantity of the chloride be agitated with about its own bulk of water, the mixture gets hot and boils.

Chlorofumaric chloride reacts with strong ammonia with great violence, and the resulting solution deposits a crystalline substance on standing. If to an ethereal solution of the chloride an ethereal solution of aniline be added energetic action takes place, a solid substance separating out; this, when crystallised from alcohol in which it is not very soluble, was obtained as pale yellow needles melting at 186—188°.

The following density determinations were made of three different preparations of the chlorofumaric chloride:—

I. From tartaric acid. B. p., 141·6—143·6°. 210 mm.

$d\frac{15^\circ}{15^\circ}$ 1·5826,

$d\frac{20^\circ}{20^\circ}$ 1·5764,

$d\frac{25^\circ}{25^\circ}$ 1·5717,

II. From tartaric acid. B. p., 143—145°. 210 mm.

$d\frac{4^\circ}{4^\circ}$ 1·5956,

$d\frac{15^\circ}{15^\circ}$ 1·5807,

$d\frac{25^\circ}{25^\circ}$ 1·5690.

III. From racemic acid. B. p., 142—144°. 210 mm.

$d\frac{4^\circ}{4^\circ}$ 1·5890, $d\frac{15^\circ}{15^\circ}$ 1·5731,

$d\frac{25^\circ}{25^\circ}$ 1·5623.

The following numbers were obtained for the magnetic rotation of this substance, Specimens II and III being used.

Specimen II. From Tartaric Acid.

t.	Sp. rotation.	Mol. rotation.
21·0°	1·5025	9·951
21·5	1·5019	9·950
22·0	1·5015	9·951
Average 21·5	1·5017	9·951

Specimen III. From Racemic Acid.

t.	Sp. rotation.	Mol. rotation.
20·2°	1·5250	10·134
20·2	1·5249	10·133
20·2	1·5269	10·145
Average 20·2	1·5256	10·137

The average of these two sets of determinations is 10·044.

Chlorofumaric Acid.

This acid, previously called chloromaleic acid, is obtained from the chlorofumaric chloride by the action of water. The aqueous solution is separated from any oily products, evaporated to a small bulk and allowed to crystallise, then drained, and pressed; if crystallised twice more it is pure. The crystallisation is much facilitated by the addition of some strong hydrochloric acid, chlorofumaric acid being much less soluble in water in presence of this acid; this is also true of its alcoholic solution. Chlorofumaric acid forms very minute prismatic crystals, and when dry looks like a white amorphous powder. It is easily soluble both in water and in alcohol. It gave the following numbers on analysis:—

0·2023 gram of substance gave 0·2376 gram of CO_2 and 0·0398 OH_2 gram.

	Theory for $C_4H_3ClO_4$.	Found.
Carbon	31·89	31·58
Hydrogen	1·99	2·18

It melts at 189—190°, or at 191·5—192·5° corr. Kauder, who has also examined this acid (*J. pr. Chem.* [2], **31**, 28), gives 191°. If kept heated so that it gently boils, it at first sublimes to a small extent, then gives off gas regularly, consisting of hydrogen chloride and about equal volumes of carbonic anhydride and carbonic oxide, most of the product disappearing.

Heated with bromine in a sealed tube at 100°, it does not combine with it.

Hydrogen Potassium Chlorofumarate.—This salt was prepared from the chlorofumaric acid obtained from tartaric acid, and also from that from racemic acid to see if they were identical: no difference could be detected. Determinations of their solubility in water gave the following numbers. Temp. = 15°.

Salt from tartaric acid; 100 parts of sol. gave 3·852 of salt.
„ racemic „ „ „ 3·834 „

For the following measurements of the crystals I am indebted to Herr V. Ussing.

Potassium Chlorofumarate Crystallised from Water.

Asymmetrical.

$$a : b : c = 0{\cdot}5223 : 1 : 0{\cdot}7910.$$

$\alpha = 91° 22'$; $\beta = 105° 55'$; $\gamma = 53° 47'$.

Forms: (010) $\infty\breve{P}\infty$; (101) $\infty\breve{P}\infty$; (001) 0P; (110) $\infty P'_1$; (011) $_1\breve{P}'\infty$; ($\bar{1}02$) $\frac{1}{2}P_1\infty$. Thin in the direction of the brachypinacoid, elongated in the direction of the axis *c*.

In individual crystals the two vertical pinacoids are equally developed. The hemiprism was only rarely observed.

	Observed.	Calculated.
(100) : (010)	122° 26′	—
(100) : (001)	71 11	—
(010) : (001)	100 16	—
(001) : ($\bar{1}02$)	77 28	—
(001) : (011)	48 7	—
($\bar{1}01$) : (011)	55 10	54° 57′

Cleavage perfect in the direction (100), less perfect in the direction ($\bar{1}02$).

The direction of extinction on (100) is inclined 15° to the left from the vertical axis: on (010) it is also inclined about 32° to the left. The optical axis cuts (100) in a line which forms an angle of 75° with the crystallographic axis *c*, to the right above; below to the left.

The trace on (010) forms an angle of about 89° with the axis *a*, to the right above; below to the left.

In Schneider's apparatus both axes are perceptible in a cleavage plane parallel to (100). The angle for the sodium line in glass is 79°.

The bisectrix is almost vertical to the macropinacoid. Strong negative double refraction.

For particulars of the preparation and properties of this salt, see *J. Chem. Soc.*, **13**, 10.

Chlorofumarate of Ammonium.—Chlorofumaric acid combines with energy with ammonia, and if an excess of the latter be left with it, it does not cause any decomposition by removing chlorine as it does in the case of the ether. On slowly evaporating the aqueous solution of this salt, it separates out in beautiful transparent well-defined crystals. They are moderately soluble in water, and neutral to test-paper, dried at 100° they do not lose weight: a determination of the chlorine in the salt gave 18·87 per cent., the formula

$$C_4HCl(NH_4)_2O_4$$

requiring 19·24. For the following measurements of the crystals of this salt I am indebted to Herr W. Mushmann.

Ammonium Chlorofumarate.

Monosymmetrical.

$$a : b : c = 1{\cdot}3892 : 1 : 1{\cdot}0059. \quad \beta = 71{\cdot}12°.$$

Crystalline forms: (100) $\infty\breve{P}\infty$; (110) ∞P; (001) $0P$; ($\bar{1}01$) $+\breve{P}\infty$, and (010) $\infty\breve{P}\infty$. The last plane rarely seen and quite small.

	Observed.		Calculated.
(100) : (110)	*52°	45′	—
(100) : (001)	*71	12	—
($\bar{1}00$) : ($\bar{1}01$)	*67	0	—
(110) : (001)	79	0	78° 49′
($\bar{1}10$) : ($\bar{1}01$)	76	21	76 19

Cleavage very perfect in the plane of symmetry; colourless; transparent.

The optical axial plane is vertical to the plane of symmetry, and almost coincident with the base (001). The axes pass through the plane of cleavage towards (010), but out of the field of vision; they are perceptible only in Schneider's apparatus.

With moderately dilute solutions of alkaline chlorofumarates neither barium, calcium, nor mercuric chloride give a precipitate, but with

strong solutions calcium chloride gives a white crystalline precipitate sparingly soluble in hot water. The colour of a solution of copper sulphate becomes darker on the addition of a chlorofumarate. Like the fumarates, chlorofumarates give with ferric chloride an amorphous, light brown or buff precipitate.

Chlorofumaric acid boiled with copper carbonate produces a turquoise-blue powder very little soluble in water. A solution of copper acetate boiled for some time with this acid deposits a dark turquoise-blue powder, seen under the microscope to consist of small crystalline nodules.

Ethyl Chlorofumarate.

This was at first prepared by gradually adding chlorofumaric chloride to alcohol, washing the resulting ethyl-derivative with water and sodium carbonate, drying it over potassium carbonate, and distilling under reduced pressure (210 mm.). A little hydrogen chloride usually came off towards the end of the distillation, the boiling point rising a little. Two specimens were analysed, one prepared with the chloride from tartaric acid, b. p. 200—202°, 210 mm., and the other with the chloride from racemic acid, b. p. 199—201·5°, 210 mm. They gave—

	Theory for $C_8H_{11}ClO_4$.	I. Ether from tartaric acid.	II. Ether from racemic acid.
Carbon	46·5	45·54	46·18
Hydrogen	5·32	5·38	5·39

These numbers show that the chloride from racemic acid gave the purer product. Their density determinations gave for I, $d\frac{15°}{15°}$ 1·2036; for II, $d\frac{15°}{15}$ 1·19845.

The magnetic rotations were determined, but as the ethers were not considered quite pure, the details are not given. No. I gave M. rot. 11·225, and No. II, 11·300.

A quantity of this ether was prepared from pure chlorofumaric acid obtained from the chloride made from tartaric acid and alcohol. On saturating the alcoholic solution with hydrogen chloride, a good deal of acid was deposited, but on standing redissolved and etherified; the ether, after being washed, treated with sodium carbonate, and dried, boiled at 202—203° at 210 mm. A little hydrogen chloride was formed, therefore the product was left over a little potassium carbonate until this was removed, and then filtered for use. A portion of this ether, when distilled under a pressure of 760 mm., boiled at 250° constantly with but little decomposition.

Henry (*Annalen*, **156**, 178) prepared this ether by acting with phosphorus pentachloride on ethyl tartrate. The boiling point he obtained was 243—245° at 735 mm., or about 245·5—247·5° at 760 mm.

The density determinations of the ethyl chlorofumarate obtained from the pure chlorofumaric acid and alcohol gave—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}2048, \qquad d\frac{15^\circ}{15^\circ}\ 1{\cdot}19372,$$

$$d\frac{10^\circ}{10^\circ}\ 1{\cdot}1990, \qquad d\frac{20^\circ}{20^\circ}\ 1{\cdot}1893,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}1849.$$

It will be seen that these numbers are lower than those obtained with the ether prepared from the chlorofumaric chloride. It may be as well to mention here that the ether obtained from the chloride prepared from tartaric acid had a slight permanent rotation to the right. One specimen in which the pentachloride of phosphorus was used in excess for the preparation of the chloride gave 15′ for column 102 mm. long; another in which less pentachloride was used gave 28′ for the same column. The ether prepared from the pure acid had a permanent rotation of 5′ 30″ for column 102 mm. long. It is difficult to say whether this rotation is due to the pure ether or not, but it appears to be so.

The magnetic rotations of this ether gave the following numbers:—

	t.	Sp. rotation.	Mol. rotation.
	19·0°	1·1785	11·365
	19·3	1·1806	11·387
	19·6	1·1794	11·377
	16·7	1·1833	11·389
	16·6	1·1838	11·392
	16·5	1·1798	11·352
Average	18·0	1·1809	11·377

Ethyl chlorofumarate has a vinous ethereal odour; cooled in ice and hydrochloric acid it does not solidify. It has rather an irritating action on the skin. Heated with aniline to boiling, chemical action sets in, and the product on cooling solidifies to a crystalline mass from which a neutral substance crystallising from alcohol can be obtained.

Ethyl Chlorofumarate and Ammonia.

When experimenting on the subject of the action of ammonia on ethyl chlorofumarate, I was not aware of the results which had been obtained by Claus and Voeller (*Ber.*, **14**, 151) in this direction, but as I have operated in a different manner to them it may be useful if I briefly give the results of my experiments.

Claus and Voeller used the same ether as I did, but called it chloromaleic ether, and their compounds are therefore called maleic-derivatives, but as the ether is now known to be ethyl chlorofumarate, their nomenclature requires altering accordingly. They employed alcoholic ammonia of a known strength and in definite quantities. My experiments were made with aqueous ammonia.

On agitating ethyl chlorofumarate with ammonia of 0·880, diluted with about three times its volume of water, it gradually dissolved, and after a time a crystalline product separated, this was washed with cold water, and examined by the microscope, when it was found to be a mixture of two substances. If dissolved in hot water acidified with hydrochloric acid, and allowed to cool, beautiful, colourless, transparent crystals separated, which appeared to be rhombohedrons, sometimes they appeared as flat prisms with bevelled edges. They contain chlorine. A nitrogen determination gave the following result :—

0·2289 gram of substance gave 14 c.c. nitrogen at 5°, and 762 mm. = 7·56 per cent. nitrogen; the formula $C_6H_8ClNO_3$ requires 7·88 per cent. This is the same substance as that obtained by Claus and Voeller, and has the constitution—

$$\begin{array}{l} COOC_2H_5 \\ | \\ CCl \\ || \\ CH \\ | \\ CONH_2 \end{array}$$

The fusing point of my preparation was 100°, that previously found was 102°. This substance has been called ethyl chloromaleamate, but should be the chlorofumaramate.

If this substance be dissolved and strong aqueous ammonia added to the solution, decomposition takes place, and on cooling yellowish needles are deposited. The same product is obtained direct from ethyl chlorofumarate by the continued action of concentrated aqueous ammonia. The product may be purified by crystallisation from water; but even when animal charcoal is used, its yellow colour cannot be altered. It gave the following numbers on analysis :—

0·1995 gram of substance gave 52·2 c.c. of nitrogen. $t = 12·5°$. Bar. 766·5.

0·1618 gram of substance gave 0·2224 gram CO_2 and 0·0808 gram OH_2.

	Theory for $C_4H_7N_3O_2$.	Found.
Carbon	37·21	37·48
Hydrogen	5·42	5·54
Nitrogen	32·55	32·34

This is the same formula as Claus and Voeller's diamide of amidomaleic acid or diamide of amidofumaric acid :—

$$\begin{array}{l} CONH_2 \\ | \\ CNH_2 \\ \| \\ CH \\ | \\ CONH_2 \end{array}$$

But Claus and Voeller say they obtained their product in colourless scales melting at 122°. My product crystallises in pale-yellow needles, and when heated strongly becomes dark in colour and decomposes with evolution of ammonia; no definite fusing point being obtainable. Its decomposing point is apparently above 180°. This discrepancy is not easy to explain.

The diamide of amidofumaric acid is sparingly soluble in cold water, moderately soluble in hot water; it also dissolves in hydrochloric acid.

On gently heating this diamide of amidofumaric acid with dilute soda, it dissolves with evolution of ammonia, and on making a silver salt from the acid produced it gave on analysis 62·34 per cent. of silver; the formula of silver amidofumarate, $C_4H_3NAg_2O_4$, requiring 62·60 per cent. This agrees with the results of Claus and Voeller, who obtained in the same way from their diamide of amidofumaric acid an acid the silver salt of which gave them 62·93 per cent. of silver. Before accepting these results as proving that the acid is amidofumaric acid, it would be well to determine the nitrogen in this product.

Chloromaleic Anhydride.

When chlorofumaric acid is gently heated with chlorofumaric chloride in an oil-bath, molecular proportions being used, hydrogen chloride begins to be freely evolved when the mixture has attained a temperature of about 125°; in the course of about an hour's heating at this temperature the product becomes quite liquid, and on raising the temperature it distils over freely as an oil at about 192°, the operation being almost complete by the time the thermometer has reached 195°. This distillation should not be conducted slowly. On

refractionating the oil thus obtained, most of it comes over between 192—195° corr., and consists of chloromaleic anhydride.

The preparation of this anhydride was also tried by acting on chlorofumaric acid with acetic chloride. On heating a mixture of these substances—the acetic chloride used containing acetic acid—at 100° in a sealed tube, a clear liquid was obtained which deposited a large quantity of brilliant, flat, prismatic crystals on cooling. On opening the tube very little hydrogen chloride was given off. The crystals were dried first on a porous plate and then over sulphuric acid in a vacuum; they then became somewhat opaque. On drying at 100°, one preparation lost 26 per cent. and another 32 per cent., chiefly of acetic acid, though there appeared to be a small quantity of acetic chloride, as the vapour passed through silver nitrate gave a small amount of precipitate of silver chloride. The dried product proved to be unchanged chlorofumaric acid. From direct experiment, acetic acid does appear to combine with chlorofumaric acid. Pure acetic chloride was next used, and a higher temperature employed, viz., 150—160°, the chlorofumaric acid dissolved, and a slightly brown solution was produced. On opening the sealed tube, hydrogen chloride was given off in abundance, and on distilling the product the boiling point gradually rose to 190—193°, the latter being the temperature at which it mostly came over; the product was chloromaleic anhydride.

When chlorofumaric acid is gently boiled in a retort, it gives off hydrogen chloride, carbonic anhydride, and carbonic acid, as already mentioned; but if heated more vigorously, at first an aqueous liquid comes over, and after a time oily drops appear, rendering the distillate milky. This oily product soon increases in quantity, coming over alone as a clear oil, which should be collected separately; when rectified, it boils regularly at about 194°, and is chloromaleic anhydride.

A specimen of this anhydride obtained by the first process given gave the following numbers on analysis:—

0·1927 gram of substance gave 0·2529 gram of CO_2 and 0·0141 gram of H_2O.

	Theory for C_4HClO_3.	Found.
Carbon	36·22	35·79
Hydrogen	0·75	0·80

The average of seven determinations of the boiling point of chloromaleic anhydride, mostly made with different preparations, gave 196·3° corr.; those taken under reduced pressure, 210 mm., gave 150—151° corr. The method of preparing it with acetic chloride appears to be the best of the three given above.

This anhydride was for a long time supposed to be an oil, as it remained liquid for several months, but on cooling it with ice and hydrochloric acid, and rubbing it with a glass rod, it was obtained in a crystallised condition fusing at about 0°. Afterwards it suddenly commenced to produce hard crystals, the temperature rising to about +30°. These were then very strongly pressed between dried calico; in this way a small quantity of an oily product was removed, and the anhydride obtained as a dry, white product resembling maleic anhydride. It fused at 34·5°, and gave on analysis the following numbers:—

0·2489 gram of substance gave 0·3320 gram of CO_2 and 0·0186 gram of H_2O.

	Theory for C_4HClO_3.	Found.
Carbon	36·22	36·37
Hydrogen	0·75	0·83

This product was fused and placed in a stoppered bottle. After standing for about a month, during which time it remained perfectly fluid, it was cooled with ice and hydrochloric acid, and well rubbed with a glass rod. It then became a crystalline mass, but remelted again before it reached 0°. On touching it with a crystal of the anhydride melting at 34·5°, the temperature immediately rose, and it became a hard mass of crystals fusing at 34·5°. I have obtained this remarkable result on several occasions, so that the anhydride appears to have two distinct fusing points lying wide apart. The higher fusing point is the one most usually obtained. The following density determinations of three specimens of pressed anhydride gave—

	I.	II.	III.	Average.
$d\frac{4°}{4°}$	1·5670	1·5682	1·5642	1·5664
$d\frac{10°}{10°}$	1·5589	1·5601	1·5561	1·5584
$d\frac{15°}{15°}$	1·5531	1·5543	1·5503	1·5526
$d\frac{20°}{20°}$	1·5478	1·5488	1·5454	1·5473
$d\frac{25°}{25°}$	1·5424	1·5438	1·5400	1·5421

The following numbers were obtained for its magnetic rotation:—

University of Michigan

I. Product with density $d\frac{15^\circ}{15^\circ} = 1{\cdot}5531$.

$t.$	Sp. rotation.	Mol. rotation.
21°	1·2744	6·066
21	1·2765	6·074
21	1·2754	6·083
Average 21	1·2754	6·074

II Product with density $d\frac{15^\circ}{15^\circ} = 1{\cdot}5503$.

$t.$	Sp. rotation.	Mol. rotation.
22·5°	1·2774	6·096
21·7	1·2786	6·098
21·0	1·2744	6·076
16·8	1·2823	6·099
16·8	1·2833	6·101
16·8	1·2793	6·082
Average 19·3	1·2809	6·092

The mean of these results is 6·083.

Fumaric Acid and Fumaric Chloride.

Fumaric chloride when boiled with fumaric acid, molecular proportions being used, reacts with it, hydrogen chloride being evolved, and the mixture gradually becoming liquid; on distilling, malic anhydride is obtained in considerable quantity; the yield being 77 per cent. of the theoretical.

Chloromaleic Acid.

Chloromaleic anhydride if left in contact with water gradually dissolves, forming a strongly acid solution; with hot water this change takes place quickly. The solution of chloromaleic acid obtained in this way, after being evaporated to a nearly syrupy condition on the water-bath, and allowed to stand, deposits the acid in tufts of crystals; these, when spread out and examined with a lens, appear as transparent plates; when viewed between Nicol prisms, they give a beautiful play of colour.

A solution of chloromaleic acid when evaporated down with strong hydrochloric acid is converted into chlorofumaric acid.

Chloromaleic acid readily combines with bromine if heated with it in a sealed tube to 100°.

Chloromaleates.

Hydrogen Sodium Chloromaleate.—This salt, which is easily soluble in water, crystallises in beautiful rosettes of transparent crystals with well-defined and brilliant faces. A specimen dried at 100° lost 23·68 per cent. of water. A sodium determination gave 10·38 per cent. sodium on the salt before drying at 100°. Theory for $C_4H_2NaClO_4,3H_2O$ requires 23·84 per cent. water and 10·155 of sodium.

Hydrogen Potassium Chloromaleate.—This is a beautiful salt, crystallising in large, brilliant, well-formed crystals. It is easily soluble in water, nearly 10 times as much so as the corresponding chlorofumarate, 100 parts of its solution at 15° containing 29·2 parts of salt. It does not lose weight when heated at 100°. The following analyses of this compound were made:—

I. 0·2514 gram of substance gave 0·2325 gram of CO_2 and 0·0282 gram of OH_2.

II. 0·3029 gram of substance gave 0·1408 gram of K_2SO_4.

	Theory for $C_4H_2KClO_4$.	Found.
Carbon	25·40	25·21
Hydrogen	1·05	1·24
Potassium	20·73	20·87

For the following crystallographic measurements of this salt I am indebted to Professor Haushöfer.

Hydrogen Potassium Chloromaleate.

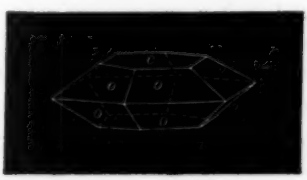
Crystal system, rhombic.

$$a : b : c = 0·4841 : 1 : 0·3479.$$

Small colourless crystals.

The combination P (111) = 0.

0P(001) = c; $2\breve{P}\infty(021) = q$. The surfaces $\infty\breve{P}\infty(010)$ are subordinate and occur but seldom as small truncations of the angle q/q.



	Observed.	Calculated.
$c : 0 = (001) : (111)$	*141° 24′	—
$0 : 0 = (111) : (1\bar{1}1)$	*148 27	—
$q : q = (021) : (02\bar{1})$	69 40	69° 40′
$0 : q = (111) : (021)$	142 40	142 49

The *neutral potassium salt* crystallises freely, but is extremely soluble and deliquescent.

Silver Chloromaleate.—This is obtained as a bulky, white precipitate on adding silver nitrate to a neutral chloromaleate. The analysis of a salt prepared in this way gave 58·97 per cent. of silver, the formula $C_4HCAg_2O_4$ requires 59·25. If an acid chloromaleate be used, this salt comes down in a crystalline condition, but from the low percentage of silver it gives on analysis it evidently contains some quantity of an acid salt. One preparation made in this way gave 56·4 per cent. of silver.

Neutral chloromaleates do not give a precipitate with ferric chloride, but produce a dark, brownish-red liquid, so that in this particular they behave like neutral maleates.

Ethyl Chloromaleate.

To prepare this, about 27 grams of silver chloromaleate were treated with an excess of ethyl iodide. The reaction did not set in to any large extent in the cold, but when the mixture was gently heated it took place vigorously, so that it was necessary to cool it. After the reaction had quieted down, the mixture was warmed on the water-bath and then allowed to remain for some time. The product was thrown on a filter, and the silver iodide formed washed several times with ethyl iodide. The filtrate was then distilled on the water-bath to remove the excess of ethyl iodide, and subsequently heated up to about 180—190°, the thermometer being in the liquid. On being fractioned under reduced pressure, it nearly all came over at 189·5—190·5° corr. at 210 mm. At 760 mm. pressure, it came over at 235°, only slight decomposition taking place. The former is about 12·5° lower than ethyl chlorofumarate, which when distilled in the same apparatus came over at 202° at 210 mm.

Ethyl chlorofumarate is a colourless oil having a pleasant odour. The specimen examined had a permanent rotation of 6′ to the right for a column 102 mm. long. Boiled with alcoholic potash, it gives an abundant precipitate of potassium chloride. It gave the following numbers on analysis:—

0·3366 gram of substance gave 0·1971 gram of CO_2 and 0·1003 gram of OH_2.

	Theory for $C_3H_{11}ClO_4$.	Found.
Carbon	46·5	46·57
Hydrogen	5·32	5·65

Its density determinations gave—

$d\frac{10°}{10°}$ 1·1872, $d\frac{20°}{20°}$ 1·1780,

$d\frac{15°}{15°}$ 1·1821, $d\frac{25°}{25°}$ 1·1740.

The following results were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
22·5°	1·1180	10·908
22·5	1·1156	10·885
22·5	1·1159	10·888
22·5	1·1153	10·882
23·0	1·1171	10·903
21·5	1·1193	10·923
21·0	1·1212	10·939
18·0	1·1250	10·943
18·0	1·1244	10·937
18·0	1·1246	10·940
Average 20·9	1·1196	10·915

The results of this inquiry show that the chloride obtained by the action of phosphorus chloride on tartaric acid is fumaric chloride, and not maleic chloride, and the acid obtained from it chlorofumaric, and not chloromaleic acid; also that chlorofumaric acid yields chloromaleic anhydride by processes similar to those by which fumaric acid yields maleic anhydride, and further, that the chloromaleic acid obtained from this is reconverted into chlorofumaric acid by heating with hydrochloric acid, just as maleic acid by the same means is changed into fumaric acid.

Chlorofumaric and chloromaleic acids also behave with bromine in a way analogous to fumaric and maleic acids, the former not combining with bromine so easily as the latter. The reaction with ferric salts is also similar, chlorofumarates giving pale-brown or buff precipitates, whilst chloromaleates give dark brown-red solutions.

With respect to other acids called chlorofumaric and chloromaleic acids, the chlorofumaric acid obtained by Bandrowski (*Ber.*, **15**, 2695) by the action of fuming hydrochloric acid on acetylenedicarboxylic acid appears to be most like the one described in this paper, but the fusing point given for it is 178°, which is considerably lower

than that of chlorofumaric acid, which is 191°. Unless there is some mistake on this point of course they cannot be identical. The acid obtained from benzene by Carius does not appear to be either the chlorofumaric or chloromaleic acid described in this paper, as it fuses at 171—172°, and its acid potassium salt crystallises with 1 mol. H_2O, moreover 100 parts of its solution at 16° contain 6·13 of dry salt, whereas the corresponding chlorofumarates and chloromaleates are anhydrous salts, and the former gives a solution containing 3·8 in the 100 parts, and the latter 29·2 at 15°.

Observations on Boiling Points.

In a paper recently published (Trans., 1888, 600), I drew attention to the great difference between the saturated and unsaturated compounds in relation to their boiling points, similar variations in composition causing opposite differences in boiling point; the comparison being between the ethers and the anhydrides, the latter in the saturated series being higher in boiling point, whereas in the unsaturated series they are lower. It may be of interest here to show how apparently inconsistent the boiling points of the unsaturated products examined in this paper and a few other allied compounds are; the densities are also given.

	B. p.	$d\frac{15°}{15°}$
Ethyl maleate*.....	223·0°	1·0740
Ethyl fumarate.....	218·5	1·0625
	−4·5°	0·0115

	B. p. 210 mm.	B. p. 760 mm.	$d\frac{15°}{15°}$.
Ethyl chloromaleate ..	190·0°	235°	1·1822
Ethyl chlorofumarate ..	202·5	250	1·1937
	+12·5	+15	+0·0115

In the case of the non-chlorinated ethers, the boiling point and densities are lower for the fumaric compounds, but in the chlorinated compounds they are greater. It is curious to notice that the difference is smaller for the boiling points taken at 210 mm.

If a comparison be made between the non-chlorinated compounds and the chlorinated, the influence of chlorination on the boiling point will be seen.

* This comparison of the boiling points of maleic and fumaric ethers is given in my previous paper (Trans., 1888, 594), but a wrong set of numbers were copied by mistake; the above are those that should have been given.

	B. p. 210 mm.	B. p. 760 mm.	$d\frac{15°}{15°}$
Ethyl chlorofumarate..	202·5°	250·0°	1·1937
Ethyl fumarate	175·0	218·5	1·0637
	27·5	31·5	0·1300
Chlorofumaric chloride.	—	186·0	1·5731
Fumaric „ .	—	162·5	1·4202
		23·5	0·1529
Chloromaleic anhydride.....		195·3	
Maleic anhydride.....		200·0	
		+4·7	

Here we find how differently chlorination affects the boiling point in the case of the anhydride, actually lowering it so that maleic anhydride has a higher boiling point than the chlorinated derivative. In the comparison of ethyl chlorofumarate with ethyl fumarate, we again find that the difference between the boiling points varies with the pressure. The differences between the densities, although not consistent, are not very wide apart, except that they vary in the reverse way to the boiling points.

If the boiling points of some of the bromine-derivatives of maleic compounds be compared in a similar way, we get—

	B. p.
Ethyl bromomaleate	256°
Ethyl maleate	225
	31
Bromomaleic anhydride.....	215°
Maleic anhydride	200
	15

In this case, the results go much in the same direction, the bromine increasing the boiling point of the ether considerably, but influencing that of the anhydride to a much smaller extent. It is, however, remarkable that ethyl bromomaleate differs in boiling point from ethyl maleate only to the same extent as ethyl chlorofumarate differs from ethyl fumarate.

Observations on Magnetic Rotations.

In considering the magnetic rotations of the substances examined in this paper, it will first be convenient to compare the molecular

rotations of the chlorinated, maleic, and fumaric ethers, and see if they are consistent with those of the non-chlorinated compounds.

	M. rot.		M. rot.
Ethyl chlorofumarate..	11·377	Ethyl fumarate.....	10·112
Ethyl chloromaleate ..	10·915	Ethyl maleate.....	9·625
Difference	0·462	Difference	0·487

These results are as close as could be expected. The following comparisons show the influence of the replacement of hydrogen by chlorine:—

	M. rot.
Ethyl chloromaleate	10·915
Ethyl maleate	9·625
Influence of Cl replacing H	1·290
Ethyl chlorofumarate.....	11·377
Ethyl fumarate	10·112
Influence of Cl replacing H	1·265
Chlorofumaric chloride	10·044
Fumaric chloride.....	8·747
Influence of Cl replacing H	1·297

These results again are quite as consistent as could be expected; the influence of the chlorine replacing hydrogen is, however, smaller than has previously been found in any other monochloro-compound, and is nearer that found when replacing a third hydrogen. The following examples will explain this:—

	M. rot.
Chloroform	5·559
Methylene chloride.....	4·313
Influence of Cl replacing H.....	1·246
Chlorethylene chloride.....	6·796
Ethylene chloride.....	5·485
Influence of Cl replacing H.....	1·311

and as the bodies under consideration represent saturated compounds less H_2, some kind of analogy can be imagined to exist between their replacement.

In a previous paper (Trans., 1888, 598), it was shown that the magnetic rotations of both maleic and citraconic anhydrides were anomalous. That of chloromaleic anhydride also does not come out

consistently. Thus, if we take the replacement of hydrogen by chlorine we get—

Chloromaleic anhydride	6·082
Maleic anhydride	4·545
Influence of Cl replacing H.....	1·537

This number is higher than that found for all other allied compounds; it seems, however, unlikely that in this compound the chlorine should have a larger value, but would lead rather to the inference that this replacement has affected the molecule of maleic anhydride, making its abnormally low rotation somewhat higher, and thus seemingly increasing the value of the chlorine it contains; even then it is lower than it apparently should be. These results again go to show that there is some peculiarity in these anhydrides which is not clear at present, and this is borne out by the remarkable character of their boiling points.

The following are some of the more important results of this inquiry.

The chloride obtained by the action of phosphorus pentachloride on tartaric and racemic acids is chlorofumaric chloride.

Chlorofumaric acid when distilled or treated with its chloride or with acetic chloride yields chloromaleic anhydride, from which chloromaleic acid and its derivatives can be obtained.

Chloromaleic acid is converted into chlorofumaric acid by heating it with hydrochloric acid, just as maleic is converted into fumaric acid.

The chloromaleic acid prepared from benzene by Carius does not agree in its properties either with chlorofumaric or chloromaleic acids.

The boiling points of the halogen-compounds of maleic and fumaric acids do not show any regular relationship to each other, those of maleic anhydride showing the greatest variations.

The magnetic rotations of chlorofumaric and chloromaleic ethers have to each other practically the same relationship as exists between those of fumaric and maleic ethers.

The effect of the replacement of hydrogen by chlorine in maleic and fumaric ethers and fumaric chloride on the magnetic rotation of these compounds is to increase them practically to the same extent, viz., by about 1·284.

The magnetic rotation of chloromaleic anhydride, although abnormal, is not so far from the calculated number as that of maleic anhydride.

LV.—*On a New Method for the Preparation of Mixed Tertiary Phosphines.*

By Norman Collie, PhD., F.R.S.E.

Since the announcement of the discovery of the phosphorus bases by Hofmann, and the subsequent publication by Cahours and himself of the classical work on this subject, now nearly 30 years ago, little has been added to our knowledge of this interesting group of substances. Michaelis has indeed investigated the aromatic phosphorus compounds, but those of the fatty series remain almost untouched. The great difficulty experienced in their preparation has doubtless acted as an obstacle to their study and preparation; still, when they have once been prepared, the simplicity and energy which characterises their reactions, and the theoretical interest attaching to many of their combinations, amply repays any time spent on the investigation of their properties.

I have already called attention (Collie, *Phil. Mag.*, July, 1887, 27), to the decomposition which some of the organic phosphonium compounds suffer when subjected to the action of heat, and in a paper by Professor Letts and myself (Letts and Collie, *Phil. Mag.*, August, 1886, 183), we first noticed the decomposition which took place when chlorides of the phosphoniums were destructively distilled:—

$$(C_2H_5)_4PCl = (C_2H_5)_3PHCl + C_2H_4.$$

This decomposition suggested a further examination of the action of heat on phosphonium chlorides, which had been found to be such an excellent practical method for obtaining a free tertiary phosphine from a quaternary compound. Hofmann has already shown how from a primary phosphine it is possible by successive additions of a hydrocarbon iodide (and subsequent liberation of the free phosphine with potash) to build up secondary, tertiary, and finally quaternary phosphonium compounds. But if we start at the other end of the series, and seek for some method by which we may retrace our steps to the original primary phosphine, we at once find the task is one by no means so easy of accomplishment. In fact, any one who has worked with these quaternary phosphonium compounds, is at once struck with the great difficulty which surrounds even the first step in the backward progress.

This decomposition of tetrethylphosphonium chloride has the advantage of being nearly a quantitative method for accomplishing this first step. Some of the oxygenated salts of tetrethylphos-

phonium yield, it is true, triethylphosphine when heated, but the chief product of their decomposition is always *the oxide of triethylphosphine*, a substance whose stability is so great that to prepare from it either triethylphosphine, or even compounds which might yield the secondary or primary phosphines, is a problem of the greatest difficulty. As these phosphonium chlorides seemed to be the only salts from which the tertiary phosphine could be obtained in any quantity, I have investigated the action of heat on several of them, chiefly in order to ascertain whether this mode of decomposition was general, and I have also used it as *a new method for the preparation of mixed tertiary phosphines*. I had wished to make the list of phosphonium chlorides experimented upon as numerous as possible, but owing to the great difficulty experienced in the manufacture of the necessary material, I have had to content myself with the salts obtainable from triethylphosphine, and a very small quantity of trimethylphosphine. All attempts to prepare tripropylphosphine were unsuccessful, as the thick glass tubes which contained the alcohols and the phosphonium iodide were usually shattered by the enormous pressure of the gases produced during the experiment. When this was not the case, only minute quantities of the phosphuretted hydrogen had entered into combination with the hydrocarbon radicles; attempts also to get the triethylphosphine to unite with chlorobenzene were without success. These two substances were heated to as high a temperature as 250°, and yet they did not combine with one another.

In the following experiment, it is shown that in the case of a large number of phosphonium chlorides, the decomposition which they suffer when heated is always the same. *Ethylene or an unsaturated hydrocarbon is formed together with a hydrochloride of a tertiary phosphine.*

When there is more than one ethyl-group present in the phosphonium chloride, ethylene is formed—

$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)PHCl + C_2H_4,$$

but when the phosphonium chloride contains only one ethyl-group, then, although ethylene is still formed, another decomposition goes on at the same time, and a mixture of two hydrochlorides results:—

$$2(C_2H_5)(CH_3)_3PCl = 2(C_2H_5)(CH_3)_2PHCl + C_2H_4.$$
$$(C_2H_5)(CH_3)_3PCl = (CH_3)_3PHCl + C_2H_4.$$

It is remarkable that if we compare the decomposition by heat of the phosphonium *chlorides*, with the decomposition of any of the ammonium salts, it must be with the *hydroxides* and not with the corresponding chlorides.

$$(C_2H_5)_4PCl = (C_2H_5)_3PHCl + C_2H_4.$$
$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)PHCl + C_2H_4.$$

$$(C_2H_5)_4N\cdot OH = (C_2H_5)_3N + C_2H_4 + H_2O.$$
$$(C_2H_5)_2(C_5H_{11})(CH_3)N\cdot OH = (C_2H_5)(C_5H_{11})(CH_3)N + C_2H_4 + H_2O.*$$

Whilst the phosphonium *hydroxides* resemble in their mode of decomposition the corresponding ammonium *chlorides*.

$$(C_2H_5)_3(C_7H_7)POH = (C_2H_5)_3PO + C_7H_8.$$
$$(C_2H_5)_2(C_7H_7)POH = (C_2H_5)_2(C_7H_7)PO + C_7H_8.$$

$$(C_2H_5)_3(CH_3)NCl = (C_2H_5)_3N + CH_3Cl.$$
$$(C_2H_5)_2(CH_3)NCl = (C_2H_5)_2(CH_3)N + CH_3Cl.†$$

In the first case, it is the ethyl-group which splits away from the molecule, whilst in the last it is any hydrocarbon radicle rather than ethyl, which parts from the nitrogen or phosphorus.

If the hydrochlorides of the tertiary phosphines are heated they probably dissociate, when in the gaseous condition, into hydrogen chloride and the tertiary phosphine; but the acid and the phosphine recombine again on cooling. In some cases the hydrochlorides of the tertiary amines behave in a similar manner, the hydrochloride of triethylamine can be distilled without decomposition, but the hydrochloride of trimethylamine decomposes when heated.

$$3(CH_3)_3NHCl = 2(CH_3)_3N + (CH_3)H_3NCl + 2CH_3Cl.‡$$

By this reaction a primary amine is produced. Up to the present this kind of decomposition has not been noticed amongst the phosphine compounds; no method for the preparation of a primary or secondary from a tertiary phosphine is known, and all attempts made in that direction have been without success.

In the phosphonium and ammonium compounds, it is usually supposed that the valency of the phosphorus and the nitrogen is pentad. This belief receives support from several facts which have been noticed during this research.

(1.) The decomposition of the mixed phosphonium chlorides, by which a mixed tertiary phosphine is produced from an ordinary tertiary phosphine.

$$(C_2H_5)_3P + C_7H_7Cl = (C_2H_5)_3(C_7H_7)PCl.$$
$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)PHCl + C_2H_4.$$

* Hofmann, *Annalen*, **78**, 283.
† V. Meyer and Lecco, *Annalen*, **188**, 177.
‡ Vincent, *Bull. Soc. Chim.*, **30**, 187.

(2.) The same mixed phosphonium salt may be prepared by two methods.

$$(C_2H_5)(CH_3)_2P + CH_3I = (C_2H_5)(CH_3)_3PI.$$
$$(CH_3)_3P + C_2H_5I = (C_2H_5)(CH_3)_3PI.$$

This kind of reaction V. Meyer has already noticed in the nitrogen series:—

$$(C_2H_5)_2NH + 2CH_3I = (C_2H_5)_2(CH_3)_2NI.$$
$$(CH_3)_2NH + 2C_2H_5I = (C_2H_5)_2(CH_3)_2NI.$$

These facts are more easily explained on the supposition that phosphorus is pentad, for a molecular change would have to occur if the valency be taken as triad.

The new phosphines that have been prepared by this method are as follows:—

	B. p.
Dimethylethylphosphine	83— 85°
Diethylmethylphosphine	110—112
Diethylpropylphosphine	146—149
Diethylisoamylphosphine	185—187
Diethylbenzylphosphine	252—255
Dibenzylethylphosphine	320—330

The difference in boiling point between the dimethylethylphosphine and the trimethylphosphine is considerably greater than between any other of the phosphines in the ethyl methyl series; if these boiling points be compared with those of the corresponding methylethylmethanes, a similar difference will be also noticed:—

	B. p.		B. p.
$(CH_3)_3P$	40— 42°	$(CH_3)_3CH$	−17
$(CH_3)_2(C_2H_5)P$	83— 85	$(C_2H_5)(CH_3)_2CH$	30
$(C_2H_5)_2(CH_3)P$	110—112	$(C_2H_5)_2(CH_3)CH$	60
$(C_2H_5)_3P$	127	$(C_2H_5)_3CH$	90

Unfortunately, comparison with the corresponding amines is impossible, as only two out of the four have been obtained.

Action of Heat on Ethyltrimethylphosphonium Chloride.

The corresponding iodide was prepared by two methods:—

(1.) By the action of iodide of ethyl on trimethylphosphine.

(2.) By the action of iodide of methyl on dimethylethylphosphine. Prepared by the first method in ethereal solution, it remained as a white, crystalline, and deliquescent solid, after the ether was evaporated.

0·351 gram gave 0·356 gram AgCl = 25·09 per cent. Cl.
Calculated for $(C_2H_5)(CH_3)_3PCl$, Cl = 25·09 per cent.

When heated it did not melt, but at a very high temperature—considerably above 300°—it decomposed, yielding a crystalline distillate and some gaseous products; 5 grams of salt were heated and 600 c.c. of gas were evolved. The gas was proved to be pure ethylene, for it was completely absorbed by bromine and gave dibromethylene, boiling at 130—134°. The distillate was acid to litmus-paper, and soluble in water. When this aqueous solution was treated with caustic soda, an oil separated; this was very volatile and had all the properties of a tertiary phosphine. It was dried and distilled; it then boiled between 40° and 60°. As there was not enough of it to separate by fractional distillation, it was treated with methyl iodide, with which it at once combined, and the resulting iodide was converted into the chloride. With chloride of platinum, a platinochloride was obtained, and on analysis gave the following numbers:—

I. 0·420 gram salt gave 0·1350 gram Pt = 32·14 per cent. Pt.
II. 0·620 „ „ 0·1996 „ = 32·19 „

The calculated percentage of Pt in $(EtMe_3P)_2PtCl_6$ is 31·55 per cent. Pt, while that required for $(Me_4P)_2PtCl_6$ is 33·05 per cent. Pt. The salt is therefore probably a mixture of the two platinochlorides: hence the chloride of trimethylethylphosphonium decomposes in two ways when heated:—

$$(CH_3)_3(C_2H_5)PCl = (CH_3)_3PHCl + C_2H_4$$
$$2(CH_3)_3(C_2H_5)PCl = 2(CH_3)_2(C_2H_5)PHCl + C_2H_4.$$

This is probable for several reasons. The gas obtained was considerably less in volume than the theoretical amount required by the first equation (600 c.c. obtained; theory 800 c.c.). Also the tertiary phosphine which was produced had no fixed boiling point (40—60°), whilst the boiling point of the trimethylphosphine is given as 40—42°.

This kind of decomposition was also noticed in the benzyl series during the experiments on the action of heat on ethyltribenzylphosphonium chloride. Moreover, the same results were again obtained from trimethylethylphosphonium chloride prepared from the product of the action of iodide of methyl on dimethylethylphosphine (p. 720). No further experiments were made with trimethylphosphine as the starting point for phosphonium chloride; the remaining salts were all produced from triethylphosphine.

Action of Heat on Triethylmethylphosphonium Chloride.

50 grams of triethylphosphine were converted into triethylmethylphosphonium iodide. The reaction was extremely violent even when the two substances were diluted with ether. The resulting iodide was converted into the chloride, from which salt a small quantity of the platinochloride was prepared for analysis.

I. 0·535 gram gave 0·152 Pt = 28·41 per cent. Pt.
II. 0·227 „ 0·203 CO_2 and 0·115 H_2O.

	Calculated for $(MeEt_3P)_2PtCl_6$.	Found. I.	Found. II.
C	24·92	—	24·38
H	5·41	—	5·62
Pt.....	28·93	28·41	—

6 grams of the chloride were heated; it decomposed above 300° without any charring, and gave a solid crystalline distillate and 760 c.c. of ethylene mixed with 40 c.c. of a gas, which was not absorbed by bromine, but which burnt with a greenish flame. The theoretical yield of ethylene, supposing the reaction to be as follows—

$$(C_2H_5)_3(CH_3)PCl = (C_2H_5)_2(CH_3)PHCl + C_2H_4,$$

would be almost 800 c.c.

The distillate was dissolved in water and treated with caustic soda; it then gave at once a free tertiary phosphine—diethylmethylphosphine. The remainder of the triethylmethylphosphonium chloride was heated, and the same phenomena were again observed. The whole of the diethylmethylphosphine obtained was dried over solid caustic soda and fractionally distilled; nearly the whole boiled between 110—112°. Its odour was similar to that of triethylphosphine; it united with sulphur and oxygen to form addition products, and with bisulphide of carbon gave red crystals.

0·332 gram gave 0·700 CO_2 and 0·3795 H_2O.

	Calculated for $(C_2H_5)_2(CH_3)P$	Found.
C.....	57·69	57·53
H	12·50	12·70

The remainder of the diethylmethylphosphine was converted into iodide of diethyldimethylphosphonium.

Action of Heat on Dimethyldiethylphosphonium Chloride.

This salt was obtained from the iodide. An analysis of the platinochloride was made.

0·450 gram gave 0·135 Pt and 0·5885 AgCl = 30·00 per cent. Pt and 32·30 per cent. Cl.

Calculated for $(Et_2Me_2P)_2PtCl_6$, Pt = 30·19 per cent., Cl = 32·97 per cent.

The remainder of the chloride of dimethyldiethylphosphonium was heated.

9 grams of salt in one experiment gave 1250 c.c. of ethylene and a solid crystalline distillate; the theoretical amount should be 1300 c.c. of ethylene, if the decomposition takes place in the following manner:—

$$(C_2H_5)_2(CH_3)_2PCl = (C_2H_5)(CH_3)_2PHCl + C_2H_4.$$

The distillate which was obtained from this and other experiments, when treated with caustic soda, gave dimethylethylphosphine, which, after drying and fractionally distilling, boiled between 83° and 85°. As there were only a few grams of this phosphine, no experiments were made with it, but the whole was converted into the iodide of trimethylethylphosphonium. This salt has already been mentioned (p. 717), but it had then been prepared by another method. The whole of it was converted into the chloride of trimethylethylphosphine. Some of the platinochloride was prepared:—

0·551 gram gave 0·1725 Pt = 31·21 per cent. Pt.

Calculated for $(Me_3EtP)_2PtCl_6$, Pt = 31·55 per cent.

This platinochloride *exactly resembled* the salt which had been prepared before. On heating the chloride of trimethylethylphosphonium, it decomposed also in a *precisely similar manner* to the chloride previously mentioned. The free phosphine obtained from the distillate boiled between 40° and 65°, and after treatment with methyl iodide and conversion into the platinochloride, it gave numbers identical with the former ones. The separation of this platinum salt into the two platinochlorides, which were supposed to be present in it, was attempted, but without any satisfactory results. The amount of the substance was very small, and both the platinochlorides seemed to be equally sparingly soluble in water.

Action of Heat on Propyltriethylphosphonium Chloride.

This salt was prepared by heating triethylphosphine for several hours with excess of chloride of propyl in a sealed tube at 130°. The

resulting white crystalline mass was dissolved in water, and separated from the excess of propyl chloride. The aqueous solution was evaporated to dryness over a water-bath. A small quantity of the platinochloride was prepared for analysis :—

I. 0·460 gram gave 0·120 Pt = 26·08 per cent. Pt.
II. 0·352 „ 0·377 CO_2 and 0·1995 H_2O.

	Calculated for $(Et_3PrP)_2PtCl_6$.	Found. I.	Found. II.
C.....	29·51	—	29·23
H	6·03	—	6·29
Pt	26·64	26·08	—

The rest of the chloride was heated. In one experiment, 2·5 grams of salt gave 300 c.c. of ethylene and a solid distillate; 2·5 grams should give 290 c.c. of ethylene, according to the following equation :—

$$(C_2H_5)_3(C_3H_7)PCl = (C_2H_5)_3(C_3H_7)PHCl + C_2H_4.$$

The distillate, together with another quantity obtained by distilling the remainder of the chloride, boiled between 225° and 228°, and gave diethylpropylphosphine when treated with caustic soda solution. After drying and distilling, this phosphine was obtained in a pure state, boiling between 146° and 149°. It united at once with ethyl iodide, to form a phosphonium iodide, which was not attacked by caustic soda. Converted into the platinochloride—

0·3615 gram gave 0·0950 Pt = 26·28 per cent.
Calculated for $(Et_3PrP)_2PtCl_6$ Pt = 26·64 per cent.

This platinochloride was exactly similar in appearance and crystalline form to one prepared from the product of the reaction of propyl on triethylphosphine.

Action of Heat on Triethylisoamylphosphonium Chloride.

When excess of isoamyl chloride (b. p. 99°), was heated at 130° in a sealed tube with triethylphosphine, a crystalline mass consisting of the triethylisoamylphosphonium chloride was obtained. This salt is very deliquescent and difficult to obtain in the form of crystals; but by heating some of it at 200° in an oil-bath, a dry salt fit for analysis was obtained.

0·414 gram took 18·0 c.c. decinormal $AgNO_3$ solution = 15·43 per cent. Cl.
Calculated for $(C_2H_5)_3(C_5H_{11})PCl$, Cl = 15·81 per cent.

Some of the platinochloride was also prepared; it is moderately soluble in water, and crystallises in thick needle-shaped crystals.

I. 0·360 gram gave 0·0385 Pt = 23·75 per cent. Pt.
II. 0·2455 gram gave 0·298 CO_2 and 0·150 H_2O.
III. 0·4925 gram gave 0·123 Pt and 0·534 AgCl = 24·97 per cent. Pt and 26·82 per cent. Cl.

	Calculated for $(Et_2AmP)_2PtCl_6$.	Found. I.	II.	III.
C.....	33·59	—	33·10	—
H.....	6·61	—	6·78	—
Pt.....	24·87	23·75	—	24·97
Cl.....	27·03	—	—	26·82

The remainder of the chloride was heated. It decomposed, at a temperature above 300°, into the hydrochloride of diethylisoamylphosphine and ethylene. The hydrochloride after redistillation boiled between 270° and 271°. On analysis—

I. 0·273 gram took 14·5 c.c. decinormal $AgNO_3$ = 18·85 per cent. Cl.
II. 0·306 gram gave 0·609 CO_2 and 0·320 H_2O.

	Calculated for $(C_2H_5)_2(C_5H_{11})PHCl$.	Found I.	II.
C.....	54·96	—	54·28
H.....	11·19	—	11·61
Cl.....	18·06	18·85	—

This hydrochloride was very deliquescent, and soluble in water. Treated with caustic soda, it gave diethylisoamylphosphine. This phosphine is a colourless, slightly viscid liquid, which does not oxidise so readily on exposure to air as the triethylphosphine, and has an odour which distinctly recalls that of fusel oil. It boils between 185° and 187°.

0·223 gram gave 0·550 CO_2 and 0·261 H_2O.

	Calculated for $(C_2H_5)_2(C_5H_{11})P$.	Found.
C.....	67·50	67·26
H.....	13·12	13·00

The decomposition which the chloride of triethylisoamylphosphonium undergoes when heated is as follows:—

$$(C_2H_5)_3(C_5H_{11})PCl = (C_2H_5)_2(C_5H_{11})PHCl + C_2H_4.$$

Action of Heat on Triethylbenzoylphosphonium Chloride.

In order to obtain this salt, triethylphosphine was warmed with a large excess of benzyl chloride. The chloride was at once formed, with evolution of a very considerable amount of heat. It was easily separated from the excess of benzyl chloride by treatment with water, and the aqueous solution on evaporation yielded this salt in the form of needle-shaped crystals. Hofmann (*Ann.*, Spl. I, 323) has prepared this salt by the action of triethylphosphine on benzylidene chloride, but it was in aqueous solution, and he only analysed the platinochloride. This chloride can be easily crystallised from an aqueous solution, but is better obtained from an alcoholic solution by precipitation with dry ether. It crystallises with 1 mol. of water of crystallisation, and melts at 178°.

2·041 grams dried in a vacuum over sulphuric acid, lost 0·137 gram = 6·71 per cent.

Calculated for 1 mol. of water of crystallisation H_2O = 6·85 per cent.

I. 0·446 gram dry salt took 19·0 c.c. of decinormal $AgNO_3$ = 15·12 per cent. Cl.

II. 0·283 gram dry salt took 11·8 c.c. of decinormal $AgNO_3$ = 14·80 per cent. Cl.

III. 0·363 gram dry salt gave 0·842 CO_2 and 0·2915 H_2O.

	Calculated for $(C_2H_5)_3(C_7H_7)PCl$.	Found. I.	II.	III.
C.....	63·80	—	—	63·26
H.....	9·00	—	—	8·92
Cl.....	14·52	15·12	14·8	—

When heated, this salt decomposed at a temperature considerably above 300°, yielding gaseous and solid products. The gas was pure ethylene, and the distillate hydrochloride of diethylbenzylphosphine. This hydrochloride boiled without decomposition between 325° and 330°, and when dissolved in water and treated with caustic soda gave benzyldiethylphosphine. An analysis of the hydrochloride was made:—

0·622 gram took 29·9 c.c. of decinormal $AgNO_3$ = 17·06 per cent. Cl.

Calculated for $(C_2H_5)_2(C_7H_7)PHCl$, Cl = 16·39 per cent.

The decomposition of the phosphonium chloride can be expressed by the following equation:—

$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)PHCl + C_2H_4.$$

A considerable quantity of diethylbenzylphosphine was prepared. On fractionation, it boiled between 250° and 255°. (During this fractionation traces of triethylphosphine were noticed.)

0·232 gram gave 0·627 CO_2 and 0·192 H_2O.

	Calculated for $(C_2H_5)_2(C_7H_7)P$.	Found.
C.....	73·33	73·70
H.....	9·44	9·19

On exposure to the air, this phosphine fumed strongly, being easily oxidised. It was converted by the action of nitric acid into the oxide of diethylbenzylphosphine, but when prepared by this method the oxide was found to be mixed with traces of nitro-compounds. It was, however, obtained pure by another process, namely, the action of heat on the hydroxide of diethyldibenzylphosphine :—

$$(C_2H_5)_2(C_7H_7)P{\cdot}OH = (C_2H_5)_2(C_7H_7)PO + C_7H_8.$$

Thus prepared it boiled between 328° and 330°, and crystallised in long needles.

0·478 gram gave 1·1785 CO_2 and 0·3675 H_2O.

	Calculated for $(C_2H_5)_2(C_7H_7)PO$.	Found.
C.....	67·34	67·24
H.....	8·67	8·54

Sodium acted on this oxide in a remarkable manner, setting free diethylbenzylphosphine.

In this respect it differs from either triethyl- or trimethyl-phosphine oxide, neither of which is acted on by sodium.

The sulphide of diethylbenzylphosphine was also prepared. Sulphur was added to an ethereal solution of the phosphine. After evaporation the sulphide remained as a crystalline mass. It is not soluble in water, but when the water is boiled it melts. It boils at a temperature between 300 and 310° with partial decomposition, and melts at 94—95°. When heated with sodium, a violent reaction takes place, and a free phosphine is produced. The remainder of the diethylbenzylphosphine was converted into diethyldibenzylphosphonium chloride by heating it with chloride of benzyl.

Action of Heat on Diethyldibenzylphosphonium Chloride.

This salt was separated from the excess of benzyl chloride, and after the aqueous solution had been evaporated it yielded crystals of this salt on cooling.

I. 0·7435 gram took 25·0 c.c. decinormal $AgNO_3$ = 11·93 per cent. Cl.

II. 0·311 gram gave 0·799 CO_2 and 0·224 H_2O.

	Calculated for $(C_2H_5)_2(C_7H_7)_2PCl$.	Found. I.	Found. II.
C.....	70·47	—	70·06
H.....	7·83	—	8·01
Cl.....	11·58	11·93	—

The platinochloride was prepared. It consists of slender needles almost insoluble in cold water, but more soluble in alcohol.

I. 1·0434 gram gave 0·2145 Pt = 20·55 per cent. Pt.

II. 0·2325 „ 0·3835 CO_2 and 0·1046 H_2O.

	Calculated for $(Et_2Bz_2P)_2PtCl_6$.	Found. I.	Found. II.
C.....	45·47	—	44·98
H.....	5·05	—	4·99
Pt.....	20·52	20·55	—

This chloride of dibenzyldiethylphosphonium decomposed when heated in a manner exactly similar to the other chlorides—

$$(C_2H_5)_2(C_7H_7)_2PCl = (C_2H_5)(C_7H_7)_2PHCl + C_2H_4,$$

but there was a small quantity of toluene formed when the solid distillate was dissolved in water. The tertiary phosphine, which was obtained from the distillate on drying and distilling, boiled at 320—330°. It was a somewhat oily liquid, which when warmed fumed on exposure to the air, and had a pleasant penetrating odour.

0·232 gram gave 0·627 CO_2 and 0·192 H_2O.

	Calculated for $(C_2H_5)(C_7H_7)_2P$.	Found.
C.....	73·70	73·33
H.....	9·19	9·44

Action of Heat on Tribenzylethylphosphonium Chloride.

Dibenzylethylphosphine was heated with excess of benzyl chloride in order to obtain tribenzylethylphosphonium chloride. This salt can be purified by recrystallisation from water. It crystallises with 1 mol. H_2O.

0·315 gram salt lost at 110° 0·015 gram H_2O = 4·76 per cent.

Calculated for $(C_2H_5)(C_7H_7)_3PClH_2O$. H_2O = 4·65 per cent.

A chlorine analysis was also made of the dry salt—

0·811 gram salt took 22·5 c.c. decinormal $AgNO_3$ solution = 9·84 per cent. Cl. Calculated for $(C_2H_5)(C_7H_7)PCl$. Cl = 9·63 per cent.

Some of the platinochloride was also prepared. This salt is very insoluble in cold water, but is more soluble in alcohol and hot water.

I. 0·2715 gram gave 0·0485 Pt = 17·86 per cent. Pt.

II. 0·1915 gram gave 0·350 Pt = 18·27 per cent. Pt and 0·152 AgCl = 19·64 per cent. Cl.

III. 0·186 gram gave 0·3478 CO_2 and 0·0837 H_2O.

	Calculated for $(EtBz_2P)_2PtCl_6$.	Found. I.	II.	III.
C	51·40	—	—	50·99
H	4·84	—	—	5·00
Pt	18·15	17·86	18·27	—
Cl	19·80	—	19·64	—

The chloride of ethyltribenzylphosphonium when heated did not decompose in at all a simple manner, and from the small quantity which was used (4 grams) no very definite results could be obtained. Ethylene was evolved, but in small quantity only; hydrogen chloride, stilbene, and a resin were also produced. The distillate was washed with water, and on adding caustic soda to the aqueous solution some diethylbenzylphosphine was liberated. Whether the resin was tribenzylphosphine or not could not be determined, for even if the amount had been larger it would have been impossible to purify it. Some years ago, in a paper published in conjunction with Professor Letts (Letts and Collie, *Trans. Roy. Soc. Edin.*, **30**, Part I, 213), the difficulty surrounding the preparation of tribenzylphosphine was pointed out; a resin was obtained where it was expected that tribenzylphosphine would be found, and when analysed this resin gave numbers agreeing fairly well with those required by tribenzylphosphine.

The decomposition of the chloride of ethyltribenzylphosphine may possibly be as follows:—

$$(C_2H_5)(C_7H_7)_2PCl = (C_7H_7)_3P + C_2H_4 + HCl$$
$$2(C_2H_5)(C_7H_7)_2PCl = 2(C_7H_7)_2(C_2H_5)PHCl + C_{14}H_{12}.$$

The resin was heated with chloride of benzyl, but not even a trace of tetrabenzylphosphonium chloride could be obtained.

The decomposition of tribenzylethylphosphonium chloride is similar to the change which takes place when trimethylethylphosphonium chloride is heated (p. 718).

LVI.—*The Chemical Actions of some Micro-organisms.*

By R. Warington.

The present research was commenced with the intention of isolating, if possible, the nitrifying organism contained in soil. In the autumn of 1886, I spent, through Dr. Klein's kindness, some time in the laboratory of the Brown Institution, learning, under his instruction, the methods usually employed for the separation of different species of bacteria. On returning to the Rothamsted laboratory, I commenced the study of five organisms—two isolated from visible growths in some of my nitrifying solutions; two obtained from soil at the Brown Institution; and one, the well-known *Bacillus subtilis*, obtained from hay.

A short time afterwards I became acquainted with the paper by W. Heraeus (*Zeit. f. Hygiene*, 1886, 193). In this communication he names seven well-known organisms:—*M. prodigiosus*, *Staphylococcus citreus*, Finkler's bacterium, the spirillum of cheese, the bacteria of anthrax and typhoid fever, and the "Wurzelförmige Bacterien," as capable of nitrifying urine, and concludes that the power of producing nitrification is by no means unusual among bacteria. In April, 1887, Dr. Klein kindly supplied me with pure cultures of 12 bacteria, including several of those specifically named by Heraeus. The study of these organisms afforded results of considerable interest, and in consequence others were from time to time supplied by Dr. Klein. The investigation thus deviated from its original intention, and became, to a considerable extent, a study of some of the chemical properties of a variety of organisms, many of them well known as pathogenic. The action of these organisms has been tested in four particulars:—1. The hydrolysis of urea. 2. Action on milk. 3. Capacity for reducing nitrates. 4. Power of producing nitrification. It is proposed, after publishing the results at present obtained, to return to the investigation originally intended, and recommence the study of the micro-organisms in soil.

The Micro-organisms Studied.

The following were received, in the state of pure cultures, from Dr. Klein:—

1. Bacillus of swine fever.
2. „ of typhoid fever.
3. „ of infantile diarrhœa.

4. Bacillus of anthrax.
5. „ of septicæmia (mouse).
6. „ „ (guinea-pig).
7. „ *subtilis* (jequirity extract).
8. „ „ (scurf of scarlatina).
9. „ *fluorescens.*
10. „ *fluorescens liquescens.*
11. „ *intestini.**
12. Spirillum, Koch's cholera asiatica.
13. „ Finkler's cholera nostra.
14. „ Deneke's cheese.
15. „ Lingard's noma.
16. *Micrococcus aureus.*
17. *Staphylococcus luteus.*
18. „ *candidus.*
19. „ *candidus liquescens.*
20. *Streptococcus scarlatinæ.*

From Dr. W. R. Smith was received :—

21. *Micrococcus ureæ.*

The following five were isolated under Dr. Klein's superintendence :—

22. *Bacillus subtilis* (hay).
23. „ *floccus.*
24. „ *toruliformis.*
25. „ *sulphureus.*
26. „ *tardecrescens.*

There was also separated from specimens of *M. prodigiosus*—

27. *Micrococcus gelatinosus.*

A considerable number of the organisms here enumerated are well known, and need no description. In some other cases a reference to the original description will suffice.

1. *Bacillus of swine fever* (Klein). See *Reports of Med. Offic. Loc. Gov. Board*, 1877–8, 169; 1886–7, 446, Pl. XXV.

3. *Bacillus of infantile diarrhœa* (Klein). See same *Reports*, 1886–7, 447, Pl. XXVII. It will be more fully described in the following *Report.*

5. *Bacillus of septicæmia, mouse* (Klein). *Ibid.*, 447, Pl. XXVI.

6. *Bacillus of septicæmia, guinea-pig* (Lingard). *Ibid*, 1885-6, 178, Plate XIX.

* When this paper was communicated to the Chemical Society the organism now called *B. intestini* was spoken of provisionally as *Bacterium termo.*

9 and 10. *Bacillus fluorescens.* These two fluorescent bacilli will be described by Dr. Klein in *Med. Offic. Report*, 1887–8.

11. *Bacillus intestini.* Obtained by Dr. Klein from the large intestine in a case of diarrhœa in a rabbit. Grown in broth it appears as a short bacillus with rounded ends. The longer forms are 1·0—1·5 μ in length, and about 0·4 μ in thickness.

In a plate culture, it appears the first day as small translucent dots, which afterwards develop in the depth to opalescent spheres, and on the surface produce a shining expanse of pearl-like lustre.

In a stabbed culture, the growth at first is chiefly in the depth. The track of the needle is bounded by rows of opaque spheres. There is no liquefaction.

In broth at 22°, or 33°, a dense white turbidity is produced, with no film.

15. *Spirillum of noma* (Lingard). This non-liquefying spirillum is described in the *Practitioner*, **38**, 121, Figs. 32—35.

18. *Staphylococcus candidus* (Klein). This non-liquefying organism was obtained from condensed milk. *Med. Offic. Report*, 1886–7, 386, No. 3.

19. *Staphylococcus candidus liquescens* (Klein). Obtained from the blood of a scarlatina patient. *Ibid.*, 370, Pl. VII.

20. *Streptococcus scarlatinæ* (Klein). *Ibid.*, 1886–7, 374, Pls. I—XII. The organism used in the experiments described in this paper was obtained from the blood of a scarlatina patient.

21. *Micrococcus ureæ* (Smith). *Quart. Jour. Micro. Science*, 1887, 371.

23. *Bacillus floccus.*—Obtained from garden soil at the Brown Institution. A straight bacillus, 3·0—7·5 μ in length, and 1·0 μ in thickness; motile, in broth forms long interlacing threads.

In gelatin plate cultures at 22°, it forms the first day faint colonies which, under a low magnifying power, resemble balls of cobweb; from these fine interlacing threads, resembling the mycelium of a fungus, spread in every direction. Liquefaction commences the first day, and on the second extends over most of the surface.

In stabbed gelatin cultures at 22°, it forms a liquefied channel in the course of the needle the first day. From this channel numerous fine branches, resembling knotted threads, pass into the gelatin. The second day liquefaction has extended over the surface; the channel has disappeared, and the gelatin is filled with finger-like branches, starting from the old tube. The fifth day liquefaction is completed. A soft, thick film forms on the surface; below this are two layers of growth with clear spaces between. These two layers finally become one, and sink to the bottom. The liquefied gelatin becomes brown near the surface.

On agar agar at 22°, a grey, finely crinkled film quickly spreads over the whole surface.

In diluted urine, or in very weak broth at 22°, it forms dense white flocks resembling those produced by anthrax, the rest of the liquid remaining clear.

In normal broth at 33°, it forms, after some days, a thick soft film, which falls as ribbons.

24. *Bacillus toruliformis.*—Obtained from garden soil at the Brown Institution. Maximum length 5·3 μ, a few 6·4 μ; thickness 1·0—1·6 μ. The ends thickened, and much rounded. Many short, thick forms joined together. The general arrangement very crooked and irregular.

In gelatin plate cultures, it forms the first day white dots, having a granular margin. The second day there are large white colonies, many $\frac{1}{16}$ or $\frac{1}{8}$ inch in diameter. Under a low magnifying power they appear of granular structure. Liquefaction has commenced.

In stabbed gelatin, the first day's growth is chiefly confined to the needle channel, and consists of moderately opaque dots. The second day liquefaction commences. It occurs principally at the surface. A funnel of liquefied gelatin is formed with a short conical pipe, and white organism in the pipe, the upper liquid being clear without film. The gelatin at the bottom of the tube remains long unliquefied.

On agar agar at 22°, it grows rapidly, forming a pasty, moderately opaque, white film.

In broth at 33°, it grows luxuriantly, producing great turbidity, an abundant fine deposit, but no distinct film.

25. *Bacillus sulphureus.*—This was isolated from a surface growth which had appeared on some solutions which had nitrified. In a deposit from dilute broth it had a length of 1—1·5 μ, and a thickness of 0·3 μ. Taken from the surface of the broth it appeared as a network of bacilli, the sheaths faintly stained, with well-stained oval dots within. The bacillus is motile.

In a plate culture, no growth appeared for several days. The colonies were at first milky points, becoming afterwards translucent spherical masses. The colour of the colonies is at first yellowish-white. By exposure to light the colonies become opaque, and of a bright sulphur colour. There is no liquefaction.

In a stabbed culture, there is scarcely any growth in the depth of the gelatin. Growth soon appears upon an inoculated surface.

In broth at 22°, it produces turbidity. After some days small clots are deposited, some strung together in ropes, together with some finer threads. Festoons of these ropes hang from the surface, but

there is no film. The deposit in broth turns yellow on exposure to light.

The bacillus does not grow at 35°.

26. *Bacillus tardecrescens.*—This organism was isolated from floating gelatinous masses occurring in some solutions of ammonium carbonate which had nitrified. Grown in dilute broth it appears as a small oval bacillus, 1·0 μ in length, and about 0·5 μ in thickness. Grown on gelatin it is somewhat smaller, and appears more like an oval coccus. It is stained by gentian-violet very slowly.

The bacillus is, under all circumstances, slow in growth. In a plate culture, the colonies became visible after a week or more; they grow into small translucent droplets, of a somewhat smoky tint.

In a stabbed culture, the growth was chiefly in the depths, it consisted of strings of spherical colonies. There was no liquefaction.

In broth, growth is slow, and only produces a very moderate turbidity.

27. *Micrococcus gelatinosus.*—Two specimens of *M. prodigiosus*, from different sources, produced a mixture of red and white growths on the surface of agar agar. The red I did not succeed in obtaining pure; the white was easily isolated by cultivation on agar agar at 35°, when the white only was developed. The white organism resembles the red in microscopical characters, but grows much better than the red at high temperatures, and preserves its vitality for a longer period.

Grown in broth, it appears as an oval coccus, or short bacillus, 0·5—1·3 μ in length, and 0·3—1·0 μ in thickness.

In plate cultures of gelatin, it appears the first day as milk-white dots, which the next day are increased to $\frac{1}{8}$ or $\frac{1}{4}$ inch diameter, and liquefied.

In stabbed gelatin, liquefaction in the channel commences the first day, and has extended over the surface by the second day. A funnel is then formed with a wide pipe. There is no film.

On agar agar it grows rapidly at 22°, less rapidly at 35°, forming a thick, pasty, whitish mass, moderately opaque, covering the whole surface.

In broth, it produces an abundant turbidity, and a considerable amorphous deposit, but no film.

General Method.

The methods of culture on gelatin, and agar agar, were those originated by Koch, and now generally employed. The nutritive gelatin, and agar agar, were of the composition employed by Dr. Klein, the former containing 10 per cent. of gelatin. The prepara-

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tion of the various liquid mediums will be described under the head of each investigation.

The microscope was one kindly placed at my disposal by the Chemical Society for the purpose of this investigation. The powers used were Zeiss' **D**, and Leitz's $\frac{1}{9^{0}}$ oil immersion lens. The stained preparations were made with gentian-violet.

All inoculations of solutions were made by means of Klein's capillary glass pipette or hollow needle, the cotton-wool stopper not being removed from the tube or bottle containing the sterilised liquid. By means of the same pipette, the acidity or alkalinity of a solution could be at any time ascertained without removing the stopper. In examining a liquid for nitrites or nitrates, a much larger pipette was employed, the capillary tube of which was passed between the stopper and the glass; sterilised wool was held against the pipette at the point where it entered the bottle, so that only filtered air might enter when suction commenced. The large pipettes were kept in boiling water till the moment when required. By proceeding in this way, the cultures were commenced and brought to a close without once removing the cotton-wool stoppers.

As a check on the results, a culture was generally made on gelatin or agar agar at the end of each experiment, or series of experiments, made in a fluid medium, the object being to prove that the action had proceeded without the entrance of any foreign organism. This check was at first employed in every case, but after confidence in the mode of work had been attained, it was made use of only to check striking or irregular results, or to ascertain the growth of an organism in milk. The method was especially necessary for the latter purpose, as successful inoculation with an organism which produced no striking change in the milk could in no other way be ascertained.

The Hydrolysis of Urea.

The hydrolysis of urea, and its conversion into ammonium carbonate, which takes place in putrefying urine, is now universally acknowledged to be due to the action of micro-organisms. Pasteur has described a micrococcus which acts in this manner. More recently (1885) Leube and Graser (*Virchow's Archiv*, **100**, 555) have separated the organisms occurring in samples of ammoniacal urine, and have found four which were capable of converting urea into ammonium carbonate. The most active of these was a short bacillus, which they name *Bacterium ureæ*. The next in activity, and the most abundant, was a micrococcus. There were besides two bacilli, which exerted a much feebler action. The authors also name a fifth

organism, "Lungen Sarcin," as capable of converting urea into ammonia. Heraeus (*Zeit. f. Hygiene*, 1886, 215, 221) isolated four bacilli which effected an ammoniacal fermentation in urine; three of these liquefied gelatin, and were therefore distinct from the organisms of Leube and Graser. During last year, Dr. W. R. Smith (*Quart. Jour. Microscopical Science*, 1887, 371) has separated about 20 organisms from ammoniacal urine, and found among them only one which was capable of producing ammonia from urea. The active organism separated by Dr. Smith was a micrococcus; it was apparently not identical with the micrococcus of Leube and Graser, as it slowly liquefied gelatin, whilst their micrococcus did not. It appears therefore that at least nine organisms are known which are capable of hydrolysing urea.

Cultivations in diluted urine have been attempted with all the organisms studied during the present investigation. Nos. 13, 14, 16, 17, and 26 have not occasioned a distinct turbidity in the solutions; Nos. 19 and 20 have given only a slight turbidity; the remainder have afforded plain evidence of growth. The urine solutions were of two kinds; the first was a 1 per cent. solution, containing gypsum, used for the experiments on nitrification. The cultures in this series of solutions were tested with Nessler's reagent after being kept for two or three weeks at 32°; the presence of gypsum in this case preventing volatilisation of the ammonia. The tint given by Nessler's reagent in the various cultures was compared with that produced by the same test in similar solutions unseeded with organisms. The organisms Nos. 1, 2, 4, 5, 11, 13, 15, 17, 18, 19, 20, 22, 23, 24, 25, and 26 were tried in this manner. In one case only (No. 18) was any distinct increase of ammonia perceived over that present in the unseeded solution.

The second urine solution contained 25 per cent. of urine, and was prepared especially to determine the action of the organisms on urea. The test-tubes containing the seeded urine were kept at the temperature of 22° for 7—10 days, the alkalinity of each cultivation was then determined by means of standard acid and alkali, and the result compared with that given by unseeded urine placed under the same conditions. The method did not admit of extreme accuracy, as the indicators employed failed to determine the point of neutrality with great exactness. All of the organisms under investigation, with the exception of Nos. 7, 8, 16, and 19, were tried by this method; in the case of 13, 14, and 17, however, no quantitative result was attempted, as there was no evidence of any growth in the solution. With the exception of two organisms, to be presently mentioned, none proved capable of distinctly affecting the alkalinity of the urine.

In the case of the *Micrococcus ureæ* (Smith), a very distinct effect

was produced on the urine. In two experiments, made with different solutions, the urine acquired a distinct ammoniacal odour. In one case the alkalinity at the end of seven days was increased to an extent equivalent to 0·0066 gram of ammonia per 10 c.c. of solution, while in the second experiment the increase of alkalinity in eight days was equal to 0·0043 gram of ammonia.

A very distinct increase in alkalinity also occurred in the case of *B. fluorescens*. In the first experiment, the increase of alkalinity in eight days was equivalent to 0·0039 gram of ammonia in 10 c.c. of the solution. In the second experiment, the increase in seven days was equal to 0·0037 gram. It seems probable from this result that the *B. fluorescens* is identical with the bacillus giving a green fluorescence obtained by Heraeus from soil, as this organism was found by him to convert urea into ammonia.

The property of effecting the hydrolysis of urea is apparently but rarely met with among micro-organisms; in the present case, out of 24 organisms tried, only two could certainly be shown to possess it. I am doubtful, however, if either of these organisms is the cause of strong ammoniacal fermentation. At all events, in two comparisons of the result produced by the *M. ureæ* with that yielded, under the same circumstances, by the mixed organisms of arable soil, the latter proved far more effective. The soil was from heavy, unmanured, arable land. The fragment used was about the size of a large pin's head; it was taken half an inch below the surface. The two comparisons were made in different solutions. The amounts of ammonia found per 10 c.c. of diluted urine were as follows:—

	Soil.	*M. ureæ*.
I.	0·0252 gram	0·0066 gram.
II.	0·0116 „	0·0043 „

It would appear probable, therefore, that the soil contained a more powerfully hydrating organism than the micrococcus of Dr. Smith; it possibly contained the active bacillus of Leube and Graser.

Action on Milk.

Milk is an excellent medium for studying the chemical action of micro-organisms, being a liquid susceptible of many changes. In all the experiments I have made, skim-milk has been employed; the inconvenience of a surface layer of cream was thus avoided. The first trials were made with skim-milk kindly supplied by the Aylesbury Dairy Company. This milk had been separated in the centrifugal machine, it was thus perfectly sweet, and as nearly as possible free from fat. The milk had, however, been sterilised by heat before it reached me, and had of course again to be heated after it had been

transferred to test-tubes. Owing probably to this double heating of the milk, it required a longer time to curdle than the milk subsequently employed. The milk afterwards used in the experiments was taken directly from the cow into a sterilised stoppered bottle; the portion collected was never the first or the last milk from the udder. The bottle of milk was stood in a cool place for 36 hours. The milk below the cream layer was then drawn off by a syphon, and 10 c.c. measured into each test-tube. The test-tubes, closed of course with sterilised cotton-wool, were then heated at 100° for 20 minutes in a steamer. Only three imperfectly sterilised tubes were observed during the whole investigation.

The precipitation of the caseïn, which determines the curdling of milk, may be brought about either by an acid, or by a soluble ferment, as rennet; the latter is capable of solidifying milk even when it has been made alkaline with sodium carbonate.

The proportion of acid required to curdle milk is smaller the higher is the temperature; thus milk that is only slightly sour may be completely curdled if heated to boiling. Attempts were made to ascertain what was the smallest proportion of lactic acid that would suffice to curdle milk. Very dilute lactic acid was slowly dropped into 10 c.c. of sterilised skim-milk; milk acidified with different proportions of acid was then heated, and the effect observed. With 0·15 gram of lactic acid per 100 c.c. of milk, a tolerably complete solidification of the milk was obtained when the test-tube was plunged into boiling water. A considerably smaller proportion of lactic acid sufficed to produce a partial curdling. With 0·32 gram of lactic acid per 100 c.c. of milk, the whole became nearly solid in two hours at 33°. The proportion of lactic acid required to curdle at lower temperatures could not be ascertained by this method, as it was found impossible to mix the necessary proportion of acid with the milk without at once curdling it, the acid being unavoidably present in great excess at the spot on which the drop of acid fell. It is difficult to determine the quantity of acid in milk with much accuracy, the reaction with litmus-paper being far from sharp. Neutral litmus-paper was used as the indicator in all the experiments.

To Hueppe (*Mittheil. a. d. k. Reichsgesundheitsamt*, 2, 309) we are indebted for the fullest study of the organisms affecting milk. He names five as capable of souring milk. One, a bacterium or bacillus, which curdles with the evolution of carbonic acid gas; two cocci obtained from the mouth; *M. prodigiosus*; and the coccus of osteomyelitis.*

* Marpmann (*Arch. Pharm.*, 1886, 243) states that he has obtained five organisms producing lactic acid from the milk supplied to Göttengen; his descriptions do not seem to be published yet.

Among the organisms which I worked with, five have distinctly acidified milk; most of these organisms are certainly different species from those enumerated by Hueppe. The acidification by these organisms has been in very different degrees. The three first named act apparently simply by the production of acid; in the case of the fourth and fifth, the action is more complicated.

Staphylococcus candidus.—At 22° this organism distinctly acidified the milk. The culture was continued for 43 days without visible change in the milk, save the production of a slight sediment.

At 32°, after eight days, the acidity of the milk was equal to 0·13 gram of lactic acid per 100 c.c. The milk was not curdled, and did not solidify when placed in boiling water.

At 33°, with another batch of milk, the acidity after 17 days was 0·15 per cent.

Bacillus intestini.—Grown in milk at 23°, it produced in 11 days an acidity equal to 0·33 per cent. of lactic acid; in 21 days an acidity of 0·33 per cent.; in 31 days an acidity of 0·33 per cent. The milk did not curdle at 23°; when the cultures were placed in boiling water they immediately solidified.

At 34° the milk became solid in two days; the acidity was then equal to about 0·35 per cent. of lactic acid.

Bacillus of Infantile Diarrhœa.—A culture at 22° has been quite fluid after 43 days, but examined at 83 days was found to be solid. The following amounts of acidity were found in experiments made at different times:—At 10 days, 0·33 per cent.; at 11 days, 0·34 per cent.; at 7 days, 0·31 per cent.; at 14 days, 0·35 per cent.; at 21 days, 0·38 per cent.; at 31 days, 0·44 per cent. of lactic acid.

At 33° the milk became solid in two days; the acidity was then 0·32 per cent.

At 36° the milk curdled in one day, and gas was distinctly produced.

No peptone was found in old cultures either of the curdled or uncurdled milk.

Micrococcus ureæ.—At 22° the milk begins to thicken in 12 days, and some days later becomes solid; the curd is, however, always soft. The acidities determined were—at 10 days, 0·17 per cent.; at 7 days, 0·16 per cent.; at 14 days, 0·24 per cent.; at 21 days, 0·22 per cent. The last-named culture was tested for peptone, but only a slight reaction was obtained.

At 33° a soft curdling takes place in 5 days. The amounts of acidity in different experiments were—at 7 days, 0·19 per cent.; at 8 days, 0·24 per cent.

Micrococcus gelatinosus.—At 10° the milk becomes solid in about 15 days. The curd afterwards very slowly shrinks, or partly dissolves. Peptone was distinctly present in the whey of an old culture.

At 23° the milk solidifies in 2 days; the amount of acid at that time is about 0·15 per cent. The curd very slowly becomes smaller; the whey then contains peptone very distinctly.

At 32° the milk curdles in 1 day; the acidity is then about 0·14 per cent.

On reviewing the results given by these five organisms, some points of interest appear. The first three organisms apparently do little more than produce lactic acid. The amount of acid produced by the second and third is considerably larger than that yielded by the first, but with each organism the proportion of acid which can be formed seems to be nearly a fixed quantity; at least after a certain acidity is reached further increase takes place with extreme slowness, so that apparently a culture of six weeks will not enable *Staph. candidus* to curdle milk at all, nor will it enable *Bacillus intestini* and the *Bacillus of infantile diarrhœa* to curdle milk at 22°. We may probably assume that when a certain proportion of lactic acid has been produced the further growth of the organism is checked, and with this the progress of chemical action. That the curdling which does take place is determined solely by the lactic acid produced appears very probable, for the amount of acidity in cultures freshly curdled at 33° of *B. intestini* and the *Bacillus of infantile diarrhœa* is practically the same as the amount found requisite to produce curdling in the previous experiments with lactic acid.

When we turn to the last two organisms, *M. ureæ* and *M. gelatinosus*, the circumstances are very different. *M. gelatinosus* is far more active in curdling milk than either *Bacillus intestini* or the *Bacillus of infantile diarrhœa*, for these fail entirely to curdle at 22°, while *M. gelatinosus* not only curdles in 2 days at 22°, but also after 15 days at 10°, and yet *M. gelatinosus* produces far less acidity than these two organisms. They fail to curdle milk at 22° with an acidity of 0·38 per cent.; *M. gelatinosus* succeeds in curdling milk at this temperature with an acidity of only 0·15 per cent.! It is clear, then, that in the case of *M. gelatinosus* some curdling agent other than lactic acid takes a considerable share in the reaction. The same may be said of the far less perfect curdling effected by *M. ureæ*, as here too the amount of acidity produced is by itself insufficient to effect the curdling which takes place. Further light is thrown on this subject by the results afforded by the next three organisms.

Bacillus fluorescens liquescens.—At 23° milk seeded with this organism thickens in 3 days, and becomes solid in 5 days. The milk is neutral at the time of curdling. The small quantity of whey at the surface exhibits a slight bluish-green colour. In a culture a month old the curd remained undissolved; it had become distinctly acid. Tests for peptone in cultures a fortnight old showed none, or a trace only.

Spirillum of Asiatic Cholera (Koch).—At 22° the milk exhibited a loose curdling in 4 days; it was then neutral. Milk made distinctly alkaline with sodium carbonate became solid in 3 days. After 25 days the milk was still solid; it had then become distinctly acid.

At 33° milk curdled firmly in 4 days; in 11 days it was slightly acid. Alkaline milk became solid in 1 day, and was then still alkaline. The curd in the last-named experiment shrank a good deal. The whey, tested after 15 days, was distinctly acid, and gave a strong reaction of peptone. Peptone was also found in smaller quantity in cultures in the ordinary milk 11 days old.*

Spirillum of Cheese (Deneke).—This organism acts but slowly on milk. At 22° a bright yellow ring forms at the surface of the milk in 4—6 days. A tough crust is then developed, giving the milk the appearance of solidification. Later, at somewhere about 11 days, the milk gelatinises. It is still neutral, and has a butyric odour. Still later the opaque jelly partially redissolves; the whey becomes slightly acid, and contains a distinct amount of peptone. In alkaline milk the gelatinisation begins in about 12 days, and gradually increases in solidity.

At 33° a similar course of change takes place, but apparently more slowly. The milk after 21 days is found to be alkaline, and little or no peptone is present.

In the case of the *B. fluorescens liquescens* and the *Spirillum of Asiatic cholera* we have clear instances of the complete curdling of the caseïn without the formation of any acid; the action is in fact similar to that produced by the ferment contained in rennet. It has been frequently assumed that when an organism does work exactly similar to that performed by a ferment, that it does so by the production of a ferment. There is at least one undoubted instance of the production of a ferment by a micro-organism, namely, the formation of invertin by yeast. According to S. Lea (*J. Phys.*, **6**, 136) the bacteria which convert urea into ammonia also act by the production of a ferment. Microphytes would thus appear to effect certain hydrolytic actions by the same agency as similar actions are accomplished in the cell sap of plants of more complex organisation. Facts and analogy thus seem to support the hypothesis that ferments are produced by bacteria; and until more certain light is thrown on the subject we may well assume with Hueppe and others, that the rennet-like curdling of milk is due to the production of a ferment.

With the information gained by the study of the last group of

* Since writing the above, Dr. Klein has informed me that the faculty of curdling milk has not been hitherto recognised as belonging to Koch's spirillum. The experiments have therefore been repeated, but with the same results. The gelatin cultures, prepared from the curdled milk as a check, gave normal growths.

organisms, we can now understand how *M. gelatinosus* and *M. ureæ* are able to curdle milk with the production of only a part of the acidity necessary to effect this purpose. They act in fact as ferment producers, as well as acidifiers.

The cheese spirillum possesses only a feeble gelatinising power; it appears to occupy an intermediate position between the group of rennet-like organisms, and the group of peptonising organisms which we have next to consider.

Hueppe names four bacilli and two cocci as capable, from his own observation, of gelatinising the caseïn, and then redissolving it with conversion into peptone. According to him this is by no means an uncommon property of bacteria; he ascribes it to the presence of two ferments, a rennet ferment and a trypsin ferment.

Peptone has been looked for in the present experiments by the application of the usual test of sodium hydrate and copper sulphate; and also by means of phosphotungstic acid, a reagent considerably more delicate. The milk to be tested was in every case placed in a small dialyser of parchment-paper; after 24 hours, the diffusate was examined for peptone. According to Vines and Green (*Phil. Trans.*, **178**, 43), dialysis is needed to avoid a confusion between peptone and hemialbumose, both of which give the same reaction with chemical tests, whilst only the first will pass through a membrane.

In the case of a large number of organisms small quantities of peptone have been found in the milk cultures, especially when they became old. The peptone is usually most abundant in cultures made at a low temperature (23°); at a higher temperature (33°), less peptone and more ammonia is found. Milk cultures have, for the same reason, more tendency to become alkaline at the higher temperature.

The following five organisms do not produce a solidification of the milk which corresponds to typical curdling, but the caseïn is more or less gelatinised, and then redissolved.

Bacillus subtilis (*hay*).—Milk cultures of this organism at 22° begin in two or three days to show a translucent space immediately below the surface. Each day this space increases, and the milk is resolved into a nearly clear liquid above and a soft jelly below, the latter steadily diminishing by re-solution. The clear liquid afterwards becomes turbid from bacterial growth. The reaction of the milk is neutral during the early stages of the reaction, but becomes strongly acid later; the odour is then pungent, and acids of the fatty series are clearly present. As soon as the separation into fluid and jelly is clearly established, peptone can be distinctly found, and it becomes abundant when the re-solution of the caseïn has made some progress.

At 33° the action commences earlier, but the re-solution of the caseïn seems to proceed more slowly than at a lower temperature.

The bacilli from scarlatina scurf, and from jequirity extract, peptonised as vigorously as the bacillus from hay.

Bacillus anthracis.—The experiments were made at 22°. The action goes through the same course as that described in the case of *B. subtilis*, the production of acids in the latter stage of the reaction did not apparently occur.

B. floccus.—The peptonising action is apparently as vigorous as with the two preceding organisms. No production of acid was observed.

Spirillum of Cholera nostra (Finkler).—The culture was made both at 23°, and at 37°. At the higher temperature the entire gelatinisation of the milk preceded the formation of a clear solution. Peptonisation was more vigorous at the lower temperature. This organism did not apparently act quite as rapidly as the three previously named.

Bacillus toruliformis.—The experiment was made at 22°. The action was considerably slower than in any of the preceding cases. The milk did not gelatinise for rather more than a week, and after 26 days one half of the jelly was still undissolved. The culture remained neutral.

The remaining organisms produced little effect on milk, although nearly all grew freely in it, as was proved by making gelatin cultures from the milk many days after it had been seeded.

Streptococcus scarlatinæ is stated by Klein to curdle milk at 37° in three days, or a little later. I obtained no curdling with this organism.

At 22° the milk became distinctly acid, but at the end of 43 days was quite fluid.

At 32° the acidity after eight days was equal to 0·07 gram of lactic acid per 100 c.c.; the milk was quite fluid, and did not curdle when placed in boiling water. A culture at 37°, continued for several weeks, was equally unsuccessful in producing curdling.

Fresh cultures on gelatin were used for inoculation in all these experiments.

On reporting these results to Dr. Klein, he informed me that the cultures of *Str. scarlatinæ* in his possession had also lost the power of curdling milk. Since then he has obtained a fresh supply of the organism, and finds that, as before, it curdles milk completely at 37°, rendering it very acid. This loss of the power of producing lactic acid during a long series of cultures on gelatin is a fact of great interest. The organism I experimented with had been grown on gelatin for a year and four months before the experiments in milk were made.

The two *Bacilli of septicæmia* make the milk distinctly alkaline, a change which is visible to the eye, as the milk loses much of its

opacity. The bacillus from the mouse acted more energetically than that from the guinea-pig. A trace of peptone was found in both cases in cultures three weeks old. The *Bacillus of swine fever*, *B. fluorescens*, and *B. tardecrescens* also slowly produce an alkalinity in milk.

The *Typhoid bacillus*, and *Staphylococcus luteus*, slowly render the milk slightly acid, without producing further change. *B. sulphureus* grew without producing any appreciable change. The *Spirillum of noma* did not grow easily in milk. I obtained a culture in alkaline milk only. It produced no apparent change. My stock of *Staphylococcus candidus liquescens*, and *Micrococcus aureus* was unfortunately dead before the milk experiments commenced.

It is of great interest when one property of an organism can be correlated with another. I venture to think that these experiments with milk enable us to do this. The whole of the organisms which fail to gelatinise milk are organisms that do not liquefy gelatin. The three organisms first mentioned in this section, which apparently simply attack the milk-sugar and produce lactic acid, are also non-liquefying. On the other hand, the whole of the organisms which act on milk as ferments liquefy gelatin. This conclusion is quite in accordance with the view already taken by some investigators, that the liquefaction of gelatin is itself an action produced by a ferment. We may venture therefore to predict that every liquefying organism will be found capable of gelatinising the caseïn of milk. This precipitation of the caseïn may take place with or without the formation of lactic acid, and with or without a subsequent re-solution of the caseïn as peptone.

Some experiments were made to see how the mixed organisms of soil would attack milk; the soil employed was a heavy loam from an arable field long unmanured.

At 10°, milk seeded with a small fragment of soil became gelatinised in nine days; the milk was then slightly acid. In 11 days, gas began to appear. Half the volume of the milk was then an opaque jelly. The odour was very bad, a circumstance that had not occurred with any culture made with pure organisms. Peptone was distinctly present.

At 22°, the milk curdled in 2—3 days, and became slightly acid. In 4 days the evolution of gas commenced, and continued active for some days. The curd slowly redissolved, and the solution contained peptone very distinctly. The reaction of the milk was for some time only slightly acid, but at the end of 5 weeks the acidity had become very large. The odour passed through various unpleasant stages, which it is difficult to describe.

Soil thus showed itself possessed of organisms acting like rennet

and trypsin ferments. It differed in action from the pure organisms tried, first by the production of much gas, and secondly by the formation of putrefactive products having a powerful odour.

The Reduction of Nitrates.

The reduction of nitrates to nitrogen in sewage, and in waters containing sewage, seems to have been first noticed by Angus Smith (*Mem. Lit. and Phil. Soc. Manchester*, 1867 [3], **4**, 56). He subsequently made many experiments on the subject, which are described in his Reports to the Local Government Board on the Pollution of Rivers, 1882 and 1884.

Schloesing in 1868 (*Compt. rend.*, **66**, 237) showed that during the fermentation of tobacco juice, or of putrefying urine, or during the lactic fermentation of sugar, any nitrate that was originally present disappeared, nitrous oxide, nitric oxide, and nitrogen gas being produced.

Schloesing further showed in 1873 (*Compt. rend.*, **77**, 353) that a vigorous reduction of nitrates to nitrogen gas occurs in moist vegetable soil, when a change of atmosphere is prevented. Muntz has shown (*Ann. Chim. Phys.*, 1887, **11**, 125) that under the same circumstances chlorates are reduced to chlorides, bromates to bromides, and iodates to iodides.

Some experiments were made by myself in the Rothamsted laboratory in 1880 (*Jour. Roy. Agri. Soc.*, 1881, 332) on the reduction of nitrates in soil. 7 lbs. of arable soil were placed in a percolator, forming a column 8 inches deep. The soil was saturated with water, and sodium nitrate, in quantity equal to a large agricultural dressing, placed on the surface. After a week, water was applied daily for nine days, in quantity sufficient to keep the surface covered, and the drainage was collected and analysed. At the end of this time nitrates and nitrites ceased to appear in the drainage water. Only 21 per cent. of the nitrates applied were recovered as nitrates and nitrites in the drainage. Large transverse fissures were formed in the soil by the production of gas.

The power of soil to reduce nitrates to nitrites, and finally to destroy the latter, nitrogen being probably evolved, was further shown by later experiments not hitherto published.

To 125 c.c. of a sterilised 40 per cent. solution of urine, contained in a bottle closed by a cotton-wool stopper, about 0·2 gram of arable soil was added, and the bottle placed in a cupboard having a temperature of about 10°. In five days, nitrites were distinctly present, resulting from the reduction of the nitrates naturally occurring in the urine. In 12 days neither nitrites nor nitrates could be found, the solution giving no reaction with diphenylamine.

To 100 c.c. of a 2·0 per cent. solution of urine, containing 1 gram of nitre per litre, about 0·5 gram of arable soil was added, the surface of the solution was covered with a thin layer of paraffin oil, and the bottle then placed in an incubator at 20°. In two days, a slight evolution of gas commenced, and nitrites were distinctly present. In nine days evolution of gas ceased. Nitrites have permanently remained in this solution.

A similar experiment was made at the same time, the only difference being that 5 grams of nitre, and 5 grams of glucose per litre were present in the solution. Gas was evolved as before, but in much larger quantity. In 11 days all nitrites and nitrates had disappeared.

In a duplicate experiment to the preceding, but conducted at a temperature of 35°, gas was evolved in one day, and ceased in four days, by which time the nitrites first formed had disappeared, and no nitrates could be found.

The oxidisable organic matter contained in the soil and urine is seen by the first two experiments to be capable of reducing only a small amount of nitrate; the addition of glucose in the last two experiments determined the reduction of a much greater quantity of nitrate, and the final disappearance of nitrite from the solution. That the reduction of nitrates is due to a reaction between the nitrates and the organic matter present has been recognised from the first by every investigator.

Meusel, in 1875 (*Jour. pharm.* [4], **22**, 430), was the first to prove that the reduction of nitrates to nitrites in natural waters is brought about by the agency of living organisms, which he pronounced to be bacteria.

Dehérain and Maquenne, in 1882 (*Compt. rend.*, **95**, 732), were the first to establish the same agency in the case of the reduction of nitrates in soil. It has, in fact, been abundantly shown that if sewage or soil is sterilised by the action of heat or antiseptics, no reduction of nitrates will take place.

The conditions necessary for the reduction of nitrates include a nourishing medium and temperature suitable for the growth of micro-organisms; also the presence of organic matter capable of oxidation. The exclusion of air is favourable to reduction, but not essential to it; thorough aëration is, however, fatal to the process. When the organism is capable of growing at a high temperature, such a temperature is most favourable to reduction. The organic matter suitable for effecting reduction is very varied. According to different observers, albuminoïds, sugar, propyl alcohol, ethyl alcohol, fats, glycerol, glycol, acetates and tartrates, are all active in this respect. The amount of reduction, if other conditions are equal, depends entirely on the quantity of oxidisable organic matter present. Thus Gayon and Dupetit found that in sewage, seeded with putrid urine,

not more than 0·1—0·2 gram of nitre per litre was reduced; while in chicken broth, seeded from the same source, 50 grams of nitre per litre could be reduced.

The products of the reduction of nitrates are very varied. The reduction may be to nitrites, to nitric oxide, to nitrous oxide, or to nitrogen. The formation of ammonia has been sometimes observed, but the evidence generally points to its origin in the decomposition of nitrogenous organic matter rather than from the reduction of nitrates. The formation of nitric oxide has been frequently noticed during the fermentation of sugar-beet molasses, when the solution is not kept sufficiently acid (*Compt. rend.*, **66**, 171, 237). The production of nitrous oxide has been observed by Dehérain and Maquenne during the reduction of nitrates by soil (*Compt. rend.*, **95**, 691, 854).

The differences in the products of reduction are determined:—1. By the conditions of the experiment; 2. By the specific nature of the acting organism. Till within the last few years all experiments have been made with mixtures of various organisms, such as naturally occur in the air of the laboratory, in sewage, or in soil. Working with such natural mixtures one is easily led to conclude that the character of the reaction depends entirely on the composition of the solution, or on the other conditions of the experiment. Thus Munro (Trans., 1886, 667) found that river-water readily oxidised ammonia to nitric acid, but after the addition of a tartrate reduction set in, and all nitrates disappeared from the solution. From such facts, some have concluded that not only the extent of reduction, but the whole difference between oxidation and reduction is simply determined by the composition of the solution. These ideas become, however, greatly modified when we become acquainted with the specific properties of the different organisms which together produce the actions in question, it then becomes evident that in many cases one stage of the work accomplished is performed by one organism, while a second stage is effected by another.

Within the last few years considerable progress has been made towards ascertaining the reducing faculty of individual species of bacteria. In 1882 Gayon and Dupetit (*Compt. rend.*, **95**, 1365) published quantitative results showing the amount of nitrate reduced in the same time by seven distinct organisms. The most active was a small, mobile bacillus, producing few spores, anaerobic. This organism, cultivated in chicken broth at 35°, with exclusion of air, reduced 9·6 grams of nitre per litre to nitrite in one day. Several other organisms only reduced at the rate of about 0·5 gram per day. In 1886, the same authors published a splendid research upon the reduction of nitrates by bacteria (*Ann. de la science agronomique*, 1885, **1**, 226).

A good abstract of this paper will be found in this Journal (Abstr., 1886, 823). The authors found that the reduction of nitrates to nitrites was a very usual property of the bacteria examined; they met with only one species (they notice 11) which could be cultivated in broth containing nitre without occasioning reduction. They state that a large class of bacteria reduce only to nitrites, no nitrogen gas being produced. They experimented with, but did not succeed in isolating in a pure state, the organism producing nitric oxide. They isolated two bacilli from sewage, which they named *Bacterium denitrificans* α and β; these reduced nitrates to nitrogen gas, nitrites being formed under most circumstances as a stage in the reaction. The action of the α-organism was under favourable circumstances very energetic, the liquid in which it is cultivated becoming covered with foam, and evolving in one day its own volume of nitrogen, the temperature at the same time considerably rising. The same organism when grown in an artificial solution, containing nitre and asparagine, produced a considerable amount of nitrous oxide; when the asparagine was omitted, no nitrous oxide was formed.

Heraeus (*Zeit. f. Hygenie*, 1886, 215) grew 10 bacteria, isolated from water and soil, in solutions containing a nitrate and sugar. Six grew well in this medium, and of these, two bacilli reduced the nitrate to nitrite and ammonia.

In the autumn of 1887, I communicated to the British Association (*Report*, 1887, 653) a preliminary account of the results obtained with 20 organisms, part of those forming the subject of the present paper.

In March of the present year, a paper was read before our Society by Dr. Percy Frankland (Trans., 1888, 373), in which the author describes the results he has obtained, respecting the reduction of nitrates to nitrites, with 32 species of bacteria, separated by himself from the atmosphere or from natural waters. The main series of experiments were made in a weak solution, containing as organic matter 0·25 gram of peptone, and 0·3 gram of sugar per litre, at the temperature of 30°. Of the organisms tried, 15 or 16 were found incapable of reducing nitrates to nitrites; it is to be remarked, however, that seven of these organisms produced either no visible growth, or a very slight turbidity. It would seem possible, therefore, that under conditions more favourable to growth the proportion of active organisms might be increased.

In the experiments with pure organisms which I have now to describe, the power of each organism to reduce nitrates has been tested in nearly every case in two solutions:—1. Beef broth containing 5 grams of potassium nitrate per litre; 2. A 20 per cent. urine solution, containing 1 gram of nitre per litre. In some cases

peptone has been added to the broth, and glucose to the urine solution; but these were for additional trials, outside the main series.

For the broth, 2 lbs. of lean beef were taken, cut small, treated with cold water, slowly heated with stirring, and finally boiled for half an hour. The filtered broth was made slightly alkaline to neutral litmus-paper by the addition of sodium carbonate, brought to boiling, and again filtered. The perfectly clear filtrate then received the necessary amount of nitre, and was diluted to 1200 c.c.

The urine solution was in some cases clarified by making it distinctly alkaline with potassium or sodium carbonate, boiling, and filtering; the filtrate was then neutralised with phosphoric acid. Urine thus prepared remains perfectly clear when heated for sterilisation, and also when it becomes alkaline, a fact of considerable advantage if the growth of an organism is to be determined by turbidity, or by the formation of a deposit in the solution. Urine so clarified is not, however, so nutritive as urine which has not been filtered after boiling.

The nitrated broth, or urine, was placed in small wide-mouthed bottles, previously baked at 140°; each bottle received 100 c.c., which nearly half filled it. The mouths were closed with plugs of sterilised cotton-wool, a paper cap tied on, and the contents of the bottles sterilised by heating for several hours at a temperature near 100°.

The trials were, as a rule, made at two temperatures; the lower one varied at different times from 20—23°, the higher from 32—35°.

The formation of nitrite was ascertained by two reagents: 1. The zinc iodide and starch solution of Trommsdorf; 2. Metaphenylenediamine. The first reagent is so extremely delicate that one is apt to conclude from its indications that a large amount of nitrate has been reduced, when in fact the amount of reduction has been extremely small; the extent of reduction has therefore always been judged from the results of the second test. No strictly quantitative determinations of the nitrous acid formed have been made.

The reducing power of each organism must be concluded mainly from its behaviour in the experiments with broth. The reduction of nitrate in the urine solutions was never large, the proportion of nitrous nitrogen very seldom exceeding 1 per million of the solution. The results with urine also varied a good deal at different times, according probably to the varying nutritive character of the solution.

With freely growing organisms the reduction of nitrate generally takes place speedily (if it occurs at all) both in broth and urine solutions, and most speedily at the higher temperature, if the organism will bear it. To avoid, however, repeated testing of the solutions, the cultures in broth at 32° to 35° were seldom examined

till at least three days old, and the cultures at 20—23° not before five days. The cultures of slowly growing organisms, and many of the cultures in urine, were allowed a longer time before examination.

Looking first at the bacilli, which form the largest class examined, I am disposed to place the following three first, as possessing the greatest power of reducing nitrates to nitrites.

Bacillus floccus.
„ *fluorescens non-liquescens.*
„ of swine fever.

In the case of these organisms, the culture in broth gave an exceedingly strong reaction with metaphenylenediamine, a large precipitation of the colouring matter taking place immediately.

Next in order stand the following eight bacilli, the cultures of which in nitrated broth gave a very strong reaction with metaphenylenediamine, but with no immediate precipitate of colouring matter.

Bacillus intestini.
„ of typhoid fever.
„ of infantile diarrhœa.
„ of septicæmia (mouse).
„ „ (guinea-pig).
„ *anthracis.*
Spirillum of Asiatic cholera.
„ of cheese.

Far removed from these in reducing power stands—

Bacillus subtilis.

The hay bacillus does not reduce nitrates in urine, even when glucose is added. In broth at 22°, there is frequently no reduction for a week or more, but generally a slight reduction afterwards occurs. In broth at 35°, a small reduction can be perceived after a few days. Reduction does not apparently occur till the broth becomes alkaline. The addition of peptone favours the reduction. The largest amount of nitrite noticed has probably not exceeded 5 parts of nitrous nitrogen per million of solution.

B. subtilis from the scurf of a scarlatina patient gave the same amount of reduction as the bacillus prepared from hay. The bacillus from jequirity extract gave a somewhat greater reduction. Frankland speaks of *B. subtilis* as giving no reduction; this is probably owing to the small amount of reduction it occasions when a feebly nutritive solution is employed.

The following six bacilli have given no reduction of nitrates to nitrites:—

Bacillus fluorescens liquescens.
„ *toruliformis.*
„ *sulphureus.*
„ *tardecrescens.*
Spirillum of cholera nostra.
„ of noma.

B. fluorescens liquescens, and *B. sulphureus*, have not been tested at a temperature above 23°, as they refused to grow in the hot incubator.

B. toruliformis, Finkler's spirillum, and the spirillum of noma, have each been grown with an attempt at complete exclusion of air, the surface of the culture-liquid being covered, after seeding, with a layer of paraffin oil; this addition did not at all prevent the growth of the organisms. The use of paraffin did not in any case determine a reduction of the nitrate. It was thought at first that the layer of oil would effectually protect the liquid from contact with oxygen, but a subsequent experiment, in which a solution of cuprous oxide in ammonia was substituted for the culture-fluid, showed that oxygen did in fact pass beneath the layer of oil. I hope at some time to try the effect of an absolute exclusion of oxygen.

Proceeding next to arrange the micrococci examined according to their reducing effect, and classifying them as far as possible on the same principles as the bacilli, we place in the first rank—

Micrococcus ureæ.
„ *gelatinosus.*
Staphylococcus candidus.
„ *luteus.*

These are apparently practically equal in efficacy to the three bacilli previously named as possessing the highest reducing power.

In the second rank stands one coccus—

Staphylococcus candidus liquescens.

Far removed from these comes—

Streptococcus scarlatinæ.

This must, for practical purposes, be classed as without a reducing power for nitrates, but in fact a trace of nitrous acid is shown by the delicate iodide test when it is cultivated for some time in nitrated broth. *Strept. scarlatinæ* has been grown covered with a layer of paraffin oil without developing further reducing powers.

One other micrococcus,

Micrococcus aureus,

has been grown in nitrated broth, with and without a layer of paraffin on the surface, without any production of nitrite.

Among the organisms examined by Frankland it was the bacilli only which exhibited reducing properties; among those now reported on, the micrococci have proved to be in many cases as powerful as the bacilli.

The table (p. 750) summarises the whole of the experiments on reduction. The letters R, R, r, tr., 0, indicate the extent of reduction observed. The letters n. gr. signify "no growth."

As already mentioned, the results in urine varied a good deal at different times, the whole period of experiment being more than a year. In some cases single experiments showed a distinct amount of nitrite by the iodide test, though none is mentioned in the table, a majority of experiments, made at other times, showing no nitrous acid. In several cases in which a large reduction occurred in broth at a low temperature, the experiment was not repeated at a high one. It may be safely concluded that in each of these cases the reduction would have been equally great at the high temperature, there being in none of these instances any difficulty of growth at a high temperature. Whenever an organism showed no, or very little, reduction, a trial was always made at both temperatures.

In several cases of small or no reduction, the experiment was repeated with an addition to the broth of 5 grams of peptone per litre; in no instance was the amount of nitrite increased by this addition, the broth being in itself sufficiently rich in organic matter. The addition of glucose to the urine was chiefly tried with organisms which afterwards proved to be destitute of reducing power; in one case in which the organism was able to reduce, its action was distinctly increased by the glucose.

The whole number of organisms reported on is 25; of these 7 were entirely without reducing power, 1 only produced a mere trace of nitrite, and 1 only a very small quantity. The remaining 16 reduced nitrates in broth with considerable vigour.

Of those which failed to reduce, one was of feeble growth, producing only a very limited turbidity in the broth, but others in the same class were among the most vigorously growing organisms examined. The power of reducing nitrates is thus in no way determined by rapidity and vigour of growth.

As far as I am able to judge, the reduction which has occurred has been simply from nitrates to nitrites, but this point can only be decided by strictly quantitative experiments. No production of gas has been observed in any of the broth cultures, although the amount of nitrate present was quite sufficient to occasion visible gas if a reduction to nitrogen had taken place. *B. floccus* was grown in broth under a layer of paraffin, with the especial object of observing any bubbles of gas that might be formed, but without any such result;

Experiments on the Reduction of Nitrates to Nitrites by various Micro-organisms.

No.		In broth.				In diluted urine.			
		20—23°.		32—37°.		20—23°.		32—37°.	
		Number of trials.	Reduction.	Number of trials.	Reduction.	Number of trials.	Reduction.	Number of trials.	Reduction.
23	*B. floccus*	1	R	2	R	3	r	2	r
9	„ *fluorescens non-liquescens*	1	R	1	R	1	tr.	1	tr.
1	„ of swine fever	1	R	—	—	2	tr.	2	r
11	„ *intestini*	1	R	—	—	2	0	2	tr.
2	„ of typhoid fever	1	R	—	—	3	0	3	0
3	„ of infantile diarrhœa	1	R	—	—	4	0	5	tr.
12	Sp. of Asiatic cholera	1	R	1	R	1	—	1	r
5	B. of septicæmia (mouse)	1	R	—	—	2	tr.	2	r
6	„ „ (guinea-pig)	1	R	—	—	2	tr.	2	r
4	„ of anthrax	3	R	2	R	7	0	6	0
14	Sp. Deneke's	2	R	2	R	3	0	2	n. gr.
22	*B. subtilis*	6	tr.	2	r	8	0	6	0
10	„ *fluorescens liquescens*	4	0	3	0	6	0	3	0
24	„ *toruliformis*	1	0	2	0	—	—	3	0
25	„ *sulphureus*	1	0	1	n. gr.	2	0	2	n. gr.
26	„ *tardecrescens*	1	0	1	0	—	—	—	—
13	Sp., Finkler's	1	0	4	0	—	—	3	0
15	„ of noma	1	0	2	0	—	—	3	0
21	*M. ureæ*	1	R	—	—	2	0	1	0
27	„ *gelatinosus*	1	R	1	R	3	0	4	tr.
17	Staph. *luteus*	2	R	2	R	1	0	1	n. gr.
18	„ *candidus*	1	R	—	—	3	0	2	0
19	„ „ *liquescens*	1	R	1	R	—	—	3	0
20	*Streptococcus scarlatinæ*	2	0	5	0	—	—	1	0
16	*M. aureus*	1	0	3	0	1	n. gr.	1	0

this bacillus, which was obtained from soil, is thus not one of the denitrifying bacteria of Gayon and Dupetit.

Another means of judging whether reduction has proceeded further than the stage of nitrite is by studying the alkalinity of the solution. If the reduction of potassium nitrate yields gaseous oxides of nitrogen, nitrogen, or ammonia, the solution must become alkaline from the formation of potassium carbonate. With the exception of the broth cultures of *Staph. candidus liquescens*, I have observations of the alkalinity of the broth cultures of each organism at the time when trial was made for nitrites; at this time, 3—10 days from starting the cultures, the reaction of the broth was slightly alkaline in cultivations of *M. ureæ* and *B. fluorescens liquescens*, and decidedly alkaline in the case of *B. fluorescens non-liquescens;* in all other cases, the broth was neutral, or, in a very few instances, feebly acid. With the exception, possibly, of the culture of *B. fluor. non-liq.*, the reduction to nitrites would, therefore, appear to have occurred without the production of nitrogen, oxides of nitrogen, or ammonia. After a considerable time, most of the broth cultures became distinctly alkaline; but this in itself is no proof of the destruction of nitrites, for many organisms render simple broth alkaline after growing in it for some time, the production of alkali being due to the destruction of the organic salts which the juice of meat contains.

As far then as this imperfect evidence goes, none of the organisms examined (with the possible exception of *B. fluor. non-liq.*) possessed the power of reducing nitrates to nitrogen, or to its gaseous oxides. That soil does actually contain organisms which are capable, under certain circumstances, of so reducing nitrates, has been confirmed by my own experiments already described (pp. 742–3).

Nitrites are not normally present in well aërated fertile soils, or at least only to that minute extent in which they can be shown by delicate tests to occur everywhere. The drainage waters collected at Rothamsted only rarely contain sufficient nitrite to give a distinct reaction with the delicate iodide test. Misapprehension has sometimes occurred on this point, as some analysts are in the habit of reporting the quantity of nitrogen present as "nitrates and nitrites," without apparently ascertaining in each case the presence of nitrites in the water.

Nitrification.

A good many investigations have been published during the last two years, having for their object the discovery of nitrifying organisms, or the farther elucidation of the process of nitrification: little success seems, however, to have attended these endeavours.

Celli and Zuco (*Gazz. chim. Italiana*, **17**, 99) found that a solution of ammonium chloride, containing $\frac{1}{1000}$ its weight of mercuric chloride, passed and repassed two or three times a day through a column of sterilised sand and calcium carbonate, gave, after a few days, a distinct reaction with diphenylamine. The amount of nitric or nitrous acid present was increased when spongy platinum was substituted for the sand. They conclude that the nitrification of ammonia in soil may take place without the intervention of an organism, although organisms may assist in nitrification.

Frank (*Forschungen auf dem Gebiete der Agrikulturphysik*, **10**, 56) expresses the opinion that nitrification is in greatest part an inorganic process. In his hands, soil which had been ignited was still capable of nitrifying ammonium chloride. Frank's experiments have been since repeated by Plath (*Landw. Jahrbücher*, **16**, 891), who comes to the opposite conclusion, that soil when sterilised has no power of oxidising ammonia.

We surely need not controvert at length these conclusions of Celli and Frank, contrary as they are to the accumulated evidence of many well-ascertained facts. I may perhaps refer to one of my own early experiments (Trans., 1878, 44), which seems to give a distinct answer to the question at issue. Similar soil was placed in three tubes, through which air was daily drawn, the air, in one case, containing a little chloroform vapour, in another the vapour of carbon bisulphide. Where air alone was aspirated, the nitric nitrogen in the soil increased from 8 to 50 parts per million; where the air contained the vapour of chloroform, or carbon bisulphide, no appreciable increase of nitric nitrogen took place.

Although, however, we may strongly hold that the nitrifying power of soil is due to the action of a living organism, we have still to explain the appearance of small quantities of nitric or nitrous acid in the experiments above mentioned. It is clear that in all such experiments the presence of traces of nitrites in the atmosphere must always be taken into account. I have already shown (Trans., 1881, 229) that distilled water cannot be freely exposed to air for any length of time without containing traces of nitrous acid, and the presence of this acid is soon manifested if the exposure takes place in a room in which coal-gas is burnt. When, therefore, an experimenter on nitrification makes use of the diphenylamine test, which gives a blue coloration with 1 part of nitric or nitrous nitrogen in 10 millions of water, or the far more delicate iodide and starch test, which will indicate 1 part of nitrous nitrogen in 100 millions of water, he will not improbably obtain a distinct reaction sooner or later, without a living organism having had any share in the operation, or indeed without any oxidation of ammonia having occurred in his solutions.

We turn next to the investigations with living organisms. Celli and Zuco isolated various organisms from the subsoil waters of Rome; these organisms were then grown in a solution containing an ammonium salt. In every case the solution after a time gave a small reaction with diphenylamine. The amount of nitrous or nitric acid did not increase during several months, even when a current of oxygen was passed through the solution. When the cultures were passed and repassed through a column of sand, the reaction with diphenylamine was distinctly increased. All the organisms tried seem to have behaved in a similar manner.

Adametz (*Forsch. Agr.-Phys.*, 1886, 381) isolated 22 organisms from soil. Four of these were grown in an ammoniacal solution. At the end of five weeks an extremely small quantity of nitric acid was present.

Heraeus (*Zeit. f. Hygiene*, 1886, 193) has conducted an investigation on nitrification in Koch's laboratory; about 29 organisms were examined. He obtained a powerful nitrification when a large quantity of soil was placed in a solution of ammonium carbonate. The bacterial skin which formed on the surface of the solution in this experiment was also very active in setting up nitrification. In 6 days the solution seeded with this skin oxidised 1·6 c.c. of indigo, and in 10 days 5·5 c.c. From this bacterial skin he isolated a bacillus, and a streptococcus; these, together with a bacillus and yeast isolated from fermenting urine, were grown in an ammoniacal solution similar to that already employed. All the solutions gave a distinct reaction for nitrous acid with the iodide and starch test, but the amount was too small to determine with indigo. About 13 organisms of well-known kinds were also grown in a 20 per cent. urine solution. Seven of these organisms produced in one day's growth in the incubator sufficient nitrous acid to give a strong reaction with the iodide and starch test. Heraeus concludes that these seven organisms, and the four previously mentioned, possess oxidising properties, and are capable of forming nitric acid.

Frank (*loc. cit.*) separated a number of organisms from soil, but failed on trial to obtain nitrification with any of them.

Leone (*Atti d. R. Accademia d. Lincei*, 1887, 37) concludes from his experiments that all micro-organisms are more or less capable, under favourable conditions, of producing nitric acid, and that the same organisms in the presence of organic matter are capable of reducing nitrates. Muntz (*Ann. Chim. Phys.*, 1887, **11**, 128) also cautiously observes, that organisms which appear identical with those which produce nitrification are capable of reducing nitrates when air is excluded.

Manly Miles (*Agricultural Science*, 1887, 102) writes as if he had

pure cultures of the nitrifying organism under experiment, but he gives no description of the organism.

P. Frankland (Trans., 1888, 389) grew 32 organisms obtained from air and water in a nutritive solution containing an ammonium salt for 40 days; he obtained in no case more than a faint indication of nitrous acid.

It seems very clear that not one of the investigators who have experimented with isolated species of bacteria has obtained in his solutions more than a trace of nitrous or nitric acid; *no one has obtained an amount that could be determined quantitatively.* Another point which generally appears is that every organism tried gives nearly the same result. The failure to obtain the nitrifying organism in a separate form is most conspicuous in the case of Heraeus. He had in his hands a bacterial skin which possessed energetic nitrifying properties; but the two organisms which he separated from this skin gave, in a solution of the same composition as that previously nitrified, nothing more than the usual trace of nitrous acid.

The statement of Heraeus that seven of the organisms examined commenced the nitrification of a 20 per cent. urine solution in one day is apparently due to a mistake. My own experiments show that a urine solution of that strength cannot be nitrified by soil without the addition of gypsum: the commencement of nitrification in a strong solution is also extremely slow (Trans., 1884, 661). The nitrous acid which so speedily appeared in his solutions was doubtless due to the reduction by the organisms of the nitrates naturally present in the urine (Trans., 1884, 669).

Celli and Zuco, Leone, and others, apparently believe that the oxidising or reducing action of an organism is determined by the conditions in which it is placed, and that the same organism is capable of discharging both functions. The capacity for exercising the entirely opposite functions of nitrification, and the reduction of nitrates, is indeed possessed by soil and by river water, mediums which contain a multitude of different organisms, but it cannot as yet be said to be proved of any single organism growing in a pure culture. The investigations of P. Frankland, and myself, have shown that all bacteria do not reduce nitrates, even under specially favourable conditions, and one that is capable of unmistakably oxidising ammonia has not apparently been at present isolated.

My own results respecting the nitrifying power of isolated organisms admit of a very brief description. It has been already stated that two of the organisms, *B. sulphureus*, and *B. tardecrescens*, had been separated from visible growths occurring in solutions which had nitrified. Two other organisms, *B. floccus* and *B. toruliformis*, had been obtained from soil. The remaining organisms had not an origin

that would suggest their possession of the nitrifying properties belonging to soil. The four organisms which appeared most likely to include one possessing nitrifying properties were submitted to several trials; 20 other organisms were mostly tried but once. Four different solutions were employed, the composition being varied with the view of obtaining growth with a minimum amount of carbonaceous matter present. The examination of the solutions extended in every case over many weeks. When a fragment of arable soil was added to any of these solutions, nitrification distinctly commenced within a fortnight, and in another fortnight all the ammonia (equal to about 25 of nitrogen per million of solution) had disappeared. None of the pure organisms experimented with gave any such result. A distinct reaction with diphenylamine was in some cases obtained, but this did not appear to grow in amount, although in such cases the examination was specially prolonged. The amount of nitric or nitrous nitrogen in the solutions did not apparently in any case exceed 1 per million, and all of this could not be attributed to the action of the organism, as the unseeded solutions in the incubator also gave some reaction with diphenylamine. When we have discounted the trace of nitrites probably obtained from the atmosphere, there is clearly very little left that can be attributed to the action of the organism. The question whether any part of the nitrate or nitrite present was produced by the organism I am unable to decide; but it is quite clear that none of the organisms examined possessed any nitrifying power in any way comparable with that possessed by soil. An organism which nitrifies as soil nitrifies has yet to be isolated.

LVII.—*Some Reactions of the Halogen Acids.*

By G. H. Bailey, D.Sc., Ph.D., and G. J. Fowler, B.Sc., the Owens College.

It had been noticed by one of us* that when phosphorus pentoxide was used for drying gases, there was in certain cases an indication that a considerable amount of gas was taken up. It was found, for instance, on passing a stream of air through phosphorus pentoxide tubes, which had been used for drying chlorine, sulphur dioxide, and hydrogen chloride respectively, that these gases continued to be carried over by the air for several hours. This was thought to arise from a mere mechanical retention of the gases, but as the quantities expelled were large, it was desirable to determine the character and

extent of the absorption. This seemed especially necessary, seeing that the problem of the reaction of dry gases on one another is one of great importance, and phosphorus pentoxide has been relied upon in experiments of a delicate nature where perfect desiccation was required.

For the purpose of determining the extent to which this retention of the gas took place, dry chlorine, hydrogen chloride, and sulphur dioxide respectively, were passed over a long layer of phosphorus pentoxide in a drying tube, which was weighed from time to time. It was found that, although the experiment was continued several hours, no marked increase of weight occurred. These observations appeared therefore to be in contradiction to those previously made.

Recently, however, we have been engaged in studying the relative values of desiccating agents, and the results which were obtained, when working with phosphorus pentoxide in particular, led us to reopen the question as to the action of this substance on gases.

Action of Hydrogen Chloride on Phosphorus Pentoxide.

Our method of experiment was to introduce into the gas over mercury a quantity of phosphorus pentoxide in a glass tube, open at both ends so as to give free access to the gas. With oxygen, hydrogen, sulphur dioxide, carbon dioxide, chlorine, and sulphuretted hydrogen, no absorption was observed, although the gases were left in contact with phosphorus pentoxide for several weeks.

With hydrogen chloride, however, a considerable absorption was noticed, and this went on from day to day, commencing very slowly, rising to a maximum, diminishing again, and finally ceasing.

Observations of the amount of absorption were made at convenient intervals, and the results are embodied in the following table, the volumes being in all cases reduced to normal temperature and pressure.

I.			II.*		
Time elapsed.	Absorption.	Rate in c.c. per hour.	Time elapsed.	Absorption.	Rate in c.c. per hour.
27 hours ...	6·8 c.c.	0·36	143 hours ..	112·6	0·72
48 „ ...	18·3 „	0·55	167 „ ..	124·4	0·57
70 „ ...	35·0 „	0·76	239 „ ..	138·6	0·19
77 „ ...	44·5 „	1·35	309 „ ..	148·5	0·14
103 „ ...	74·3 „	1·16	452 „ ..	158·5	0·07
119 „ ...	95·3 „	1·28	572 „ ..	163·7	0·04

* Readings in the second series of observations after the P_2O_5 tube had been in a vacuum (see p. 757).

The slow rate of absorption during the time of the first few observations is worthy of remark; though it may merely indicate that it was necessary for the hydrogen chloride to expel the air mechanically retained by the phosphorus pentoxide, before it could come into intimate contact with the latter. This would also explain why no marked increase in weight was observed when the gases were simply passed over a layer of phosphorus pentoxide.

The next question was, to determine what was the nature of the action which took place between the hydrogen chloride and the phosphorus pentoxide. That this was something more than a mere mechanical retention of the gas was indicated by the fact, that when the phosphorus pentoxide was taken out of the hydrogen chloride absorption tube and left in a Torricellian vacuum for some days, no gas was given off. The phosphorus pentoxide was therefore again placed in an atmosphere of hydrogen chloride, and, as seen from Table II, continued to take up more of the gas.

The only similar case of reaction with phosphorus pentoxide is, as far as we are aware, that noticed by Gladstone (*J. Chem. Soc.*, 1866, **19**, 290, and 1868, **21**, 64),* in which dry ammonia is taken up with formation of diamidopyrophosphoric acid.

To determine quantitatively the amounts of phosphorus pentoxide and hydrogen chloride which enter into the reaction, well-stoppered bottles were filled by displacement with hydrogen chloride, and a quantity of phosphorus pentoxide quickly inserted from a weighed tube. The amount of pentoxide added was thus known. The bottles were opened from time to time under mercury until there was no further absorption; at this stage, all the phosphorus pentoxide had become liquid. The amount of the absorption was thus measured.

As an instance of the results obtained by this method, the following numbers may be given:—Phosphorus pentoxide taken = 0·1255 gram, hydrogen chloride absorbed = 28·5 c.c., that is, 1 gram of phosphorus pentoxide takes up 227 c.c. of hydrogen chloride.

These numbers agree very nearly with the equation—

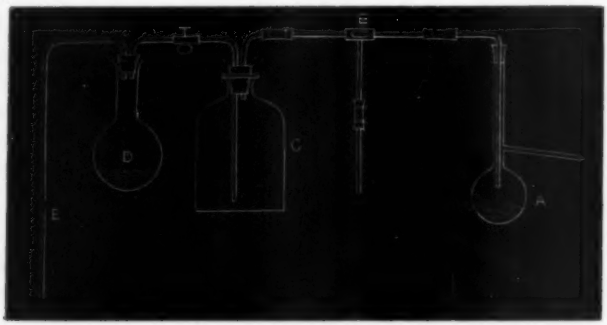
$$2P_2O_5 + 3HCl = POCl_3 + 3HPO_3.$$

Calculating from this equation, 0·1255 gram phosphorus pentoxide should take up 29·7 c.c. of hydrogen chloride; a result which agrees

* Professor Thorpe has called our attention to the fact that Mallet (*Chem. News*, **44**, 164) had observed that hydrogen fluoride was taken up by phosphorus pentoxide, from which he concluded that the pentafluoride of phosphorus was formed. Moissan has however shown (*Ann. Chim. Phys.* [6], **12**, 486) that phosphorus trifluoride combines readily with oxygen, forming a stable oxyfluoride, POF_3, analogous to the oxychloride, and it would thus seem very probable that the retention of hydrogen fluoride observed by Mallet was due to the formation of this oxyfluoride.

very nearly with that found, especially when we take account of the small errors inherent in the method of experiment.

It was difficult in this way to obtain a sufficient quantity of the compound to determine its nature. An apparatus such as is shown in the figure was therefore constructed, and as this form, which our experiments showed to be most convenient, may be found useful in cases where a regulated supply of gas free from air is required, we describe it.



A is a fractionating bulb, into which a quantity of phosphorus pentoxide was introduced, B is a three-way tap, C a large bottle serving as a reservoir for the hydrogen chloride, and D a flask containing sulphuric acid and common salt. After attaching the bulb A, containing the pentoxide, the whole apparatus was filled by displacement with hydrogen chloride, and the side tube of A sealed up. Any excess of hydrogen chloride may escape by the tube E dipping under mercury. The whole apparatus is thus sealed off from the air. The course of the reaction may be examined by allowing the vertical limb of the three-way cock B to dip under mercury, which thus showed how the absorption was proceeding. By means of the three-way tap, supplies could be drawn periodically from the reservoir to replace the gas taken up by the phosphorus pentoxide, and the reservoir could be replenished by warming the flask D.

When the reaction appeared complete, the bulb A was detached, a thermometer introduced, and the liquid distilled off, precautions being taken to prevent ingress of moisture. The liquid boiled at 108°, and showed all the properties of phosphorus oxychloride. A residue of metaphosphoric acid was left in the bulb.

From these experiments it appears that a reaction, analogous to that of Kolbe and Lautemann (*Annalen*, **113**, 240) for obtaining phosphorus oxychloride, occurs spontaneously when hydrogen chloride is left in contact with phosphorus pentoxide, and is complete if sufficient time be allowed.

Having established, therefore, the reaction in the case of hydrogen chloride, it was interesting to observe what took place in the case of the other halogen acids. These were experimented on in the same way. In the case of hydrogen bromide, absorption took place and the phosphorus pentoxide became liquid, the reaction beginning slowly and increasing to a maximum, as in the case of hydrogen chloride. Complete absorption, however, is effected much more slowly in the case of hydrogen bromide.

With hydrogen iodide, no absorption could be observed, so that although the circumstances seem especially favourable for the production of an oxy-compound, no such body is formed.

Action of Hydrogen Chloride on Mercury in presence of Oxygen.

Although it is known that hydrogen chloride has no action on mercury, it had been noticed that in some of the experiments with this gas, the mercury had been attacked, and this occurred only where oxygen was present.

Richardson has recently shown (Trans., 1887, 801), that hydrochloric acid, when mixed with excess of oxygen and exposed to light, yields chlorine; but we found that, even with small quantities of oxygen, the mercury was attacked, and became coated with a white salt.

48 c.c. hydrogen chloride and 30 c.c. oxygen, dried over calcium chloride, were introduced along with a small quantity of mercury into a stoppered vessel and exposed to diffused daylight for three weeks to allow of the reaction reaching its limit.

The vessel was then opened under mercury. Only 5 c.c. of gas remained, and the whole of the hydrogen chloride had disappeared, as there was no further absorption on the introduction of water. The chlorine had manifestly been taken up by the mercury, and oxygen equal to half the volume of the hydrogen chloride had disappeared, part of which only could have combined with the hydrogen.

In order to obtain a quantity of the mercury compound, a large cylinder was filled with a mixture of hydrogen chloride and oxygen, and a few globules of mercury introduced. The mercury was frequently shaken to renew the surface, the charge of hydrogen chloride being renewed from time to time. When sufficient of the compound appeared to be formed, it was collected, and any globules of mercury adhering to it were removed as completely as possible by amalgamation with silver. Analysis, however, showed that the compound still contained free mercury.

The analysis was performed by heating the substance (previously

dried over phosphorus pentoxide) with quicklime, collecting and weighing the mercury, and estimating the chlorine in the residue.

0·2890 gram substance yielded 0·2347 mercury.
0·0359 chlorine.

The difference, 0·0184, could consist only of oxygen or water. This evidence, taken in conjunction with that derived from the volumes of the gases concerned in the reaction, lead to the equation—

$$2Hg + 2HCl + O_2 = Hg_2OCl_2H_2O.$$

It seems, therefore, that in such an experiment there is formed an oxychloride resembling the oxycyanide, $Hg_2O(CN)_2$.

Berthelot, we found (*Ann. Chim. Phys.* [5], **23**, 100), had already noticed that mercury was attacked in some cases by hydrogen chloride, and set down the compound formed as calomel, but gives little experimental evidence in support of this.

The reaction proceeds in the dark as well as when exposed to light, and indeed powerful sunlight seems, if anything, unfavourable to it.

It was found by these experiments that if excess of oxygen is present, all the hydrogen chloride is used up, and *vice versâ*. If, however, a considerable amount of nitrogen is present as when air is mixed with the hydrogen chloride, the reaction proceeds much more slowly, and all the oxygen is not taken up even in presence of considerable excess of hydrogen chloride.

The reaction of course goes on much more slowly if excess of hydrogen chloride is present. In one case, a mixture containing only 9 per cent. of oxygen was left in contact with mercury; at the end of three weeks, nearly half the oxygen remained, the total amount of gas entering into combination being only 20 c.c. out of the 150 c.c. used.

Action of Hydrogen Bromide and Hydrogen Iodide on Mercury.

A mixture containing 33 vols. of oxygen to 45 of hydrogen bromide was taken and kept in contact with mercury in the dark. The whole of the hydrogen bromide was found to have disappeared, 37 c.c. of gas remaining. On testing this gas for oxygen with a glowing splinter, a powerful detonation occurred, showing the presence of a considerable quantity of free hydrogen; it appeared, in fact, that whereas in the case of hydrogen chloride the whole of the hydrogen combined with the oxygen, with hydrogen bromide only part of it was thus transformed.

Hydrogen iodide, as is well known, acts directly on mercury; the green mercurous iodide is first formed very rapidly, and this is converted by excess of hydrogen iodide into the red iodide. This

takes place even if the mercurous compound has been dried at 100°. The mercuric iodide is reconverted into the mercurous compound on adding excess of mercury.

Chlorine, if allowed to act on mercury in the cold, forms mercuric chloride, even in presence of a considerable excess of mercury.

Whilst the work was proceeding, we communicated with Dr. Richardson, thinking that he might have made some observations in the same direction, and we have to acknowledge the great courtesy with which he placed such facts as he had noticed at our disposal, desiring that they should appear in conjunction with ours. We cannot do better than quote his words: "Mercury in contact with hydrobromic acid and hydriodic acid (in presence of oxygen) readily decompose in the light, also, however, in the dark." "Hydrobromic and hydriodic acids, dry and free from oxygen, were almost completely decomposed in the dark; copper completely decomposes hydriodic acid."

The reactions observed open out an interesting field for studying the course of chemical reaction, and one in which we look forward with interest for the results of Dr. Richardson's investigations of the part played by light in these phenomena.

LVIII.—*The Action of Potassium on Tetralkylammonium Iodides.*

By C. M. Thompson and J. Tudor Cundall.

According to Weyl (*Watts's Dictionary*, **5**, 329), when potassium in solution in anhydrous liquefied ammonia acts on ammonium chloride, ammonium in the free state is produced, and dissolves in the ammonia, forming a blue solution. This statement lacks confirmation, and has been contradicted by Seeley (*Chem. News*, **23**, 169).

It seemed possible that more decisive results might be obtained by using some tetralkylammonium-compound instead of ammonium chloride, since just as the tetralkylammonium hydrates are easily obtainable whilst ammonium hydrate is not, so the free tetralkylammonium might be more stable that ammonium, and in any case the products of the reaction would be more easily separated and examined.

We experimented first with tetramethylammonium iodide. Some of this substance was inclosed with excess of metallic potassium in one limb of a sealed V-tube about 1 to 1½ cm. in diameter, the other limb

of which contained ammoniated silver chloride. In preparing this latter compound care was taken to exclude water as completely as possible. Nevertheless we found that some was present, and in order to dry the ammonia before condensation a quantity of sodium chips were placed between plugs of glass-wool immediately over the silver-compound.

aaa. Plugs of glass wool.
b. Bent-up capillary tube.
A. Ammoniated silver chloride.
B. Sodium chips.
C. Potassium and organic iodide.

The tubes were left sealed up for two or three days before distilling over the ammonia, so as to allow time for the sodium to remove the traces of water.

The potassium was placed in a separate small tube, so that its solution in the ammonia did not at once come in contact with the iodide. On spilling some of the blue solution on the iodide, no apparent change could be observed when the above precautions as to the removal of water were taken, although in previous experiments when traces of water were present rapid decolorisation with evolution of gas took place.

After the potassium solution and the iodide has been mixed, the tube was left at the ordinary temperature for some hours, in which time the ammonia was almost entirely reabsorbed by the silver chloride. On opening the tube, the pressure observed was not very great, and the odour of trimethylamine could be detected notwithstanding the strong smell of ammonia.

The residue in the tube was treated with alcohol, which would convert the excess of potassium and any trimethylammonium which might have been formed into alcoholates. The greater part of the tetramethylammonium iodide was left undissolved and quite unchanged by this treatment although excess of potassium was present. It was collected on a filter, and in one case weighed 3·3 grams, 5 grams having been originally employed.

The strongly alkaline filtrate was neutralised with hydriodic acid and evaporated. In the solid residue, we could detect nothing but potassium iodide. A portion of the gas contained in the tube was collected after passing through dilute hydrochloric acid. The results got on explosion with excess of oxygen and absorption of carbon dioxide by potash indicated that it consisted of a mixture of hydrogen, ethane, and nitrogen.

The ammoniated silver chloride left in the tube was heated, and the gas evolved absorbed by dilute hydrochloric acid. This solution was mixed with the hydrochloric acid solution got in purifying the gas and the whole evaporated to dryness. The solid was extracted with alcohol, the solution evaporated, and the residue converted into platinochloride.

The quantity of salt obtained from one tube was too small to divide into fractions. It contained 42·6 per cent. platinum, whilst ammonium platinochloride contains 44 per cent., showing that trimethylamine is probably present.

Whilst, therefore, the greater portion of the tetramethylammonium iodide remains unchanged, a part is acted on by the potassium, giving potassium iodide, ethane, and trimethylamine. Tetramethylammonium, if formed at all, is, under the conditions of the experiment, unstable.

As the results got with tetramethylammonium iodide were unsatisfactory, we performed another series of experiments with phenyltrimethylammonium iodide. This substance was easily prepared by bringing together dimethylaniline and methyl iodide in molecular proportion, and was purified by crystallising from water, heating with aqueous sodium hydrate to decompose hydriodides, washing well with alcohol, and finally crystallising from alcohol. Since the iodide is insoluble in ether, it might be better after washing out the sodium hydrate to wash thoroughly with ether. That the substance which we employed was pure was shown by the fact that it was odourless and that the aqueous solution gave no turbidity on warming with sodium hydrate.

5 grams of the carefully dried iodide were treated with excess of potassium in a sealed tube as before. On allowing the potassium solution to come in contact with the iodide, the blue colour was at once changed to brown. After the action was complete the tube contained two liquids, one brown and wetting the glass, the other showing a red metallic lustre like that of copper, and running about in globules like mercury. The latter liquid is exactly like a strong solution of potassium in ammonia as described by Seeley and repeatedly obtained by us.

The tubes had to be left for some time before the ammonia was

reabsorbed, for the brown liquid checked its evaporation. On opening they showed only a slight pressure, and the escaping gas smelt strongly of trimethylamine.

A portion of the gas was washed with dilute sulphuric acid, transferred to a eudiometer, and exploded with excess of oxygen. Addition of potash then caused only a slight diminution of volume. Calculating on the assumption that the whole of the carbon dioxide is derived from ethane, the rest of the gas consisting of hydrogen and nitrogen, we found the percentage of ethane in one case to be 8·15, in another 13·2. Since the total quantity of gas, free from ammonia, which could be got from one tube containing 5 grams of iodide did not exceed 100 c.c., the quantity of hydrocarbons formed in the reaction is exceedingly small, and may be the result of some secondary reaction.

The end of the tube was cut off, and the residual products of the reaction were extracted with dry ether. On evaporating the ether a liquid was left which boiled at 187—188° (uncorr.), and on heating with benzotrichloride and zinc chloride gave malachite-green. It was therefore dimethylaniline. In one case, from 5 grams phenyltrimethylammonium iodide we obtained 1·1 gram, though some was undoubtedly lost during the evaporation of the ether.

The residue, after extracting with ether, was treated with cold absolute alcohol. A crystalline substance was left which was found to be pure potassium iodide. The alcoholic solution was neutralised with sulphuric acid, and the potassium sulphate, which was free from organic matter, was filtered off and the filtrate evaporated. It gave a residue which consisted of unchanged phenyltrimethylammonium iodide mixed with a small quantity of resinous substance soluble in ether.

By heating the silver compound contained in the tube, a gas was given off which was absorbed by dilute hydrochloric acid. The solution got in this way from one tube containing 5 grams of the iodide was evaporated and the residue extracted with alcohol. The aqueous solution of the salts soluble in alcohol was precipitated by platinum chloride in five fractions. The first three on analysis gave numbers showing that they consisted of ammonium platinochloride. The fourth and fifth contained 37·2 and 37·9 per cent. of platinum respectively, the calculated percentage for $(NMe_3)_2,H_2PtCl_6$ being 37·0. Whilst these fractions were being heated, a strong smell of trimethylamine was observed, so that there can be no doubt as to the nature of the substance. The two fractions weighed 0·778 gram, containing 0·173 gram trimethylamine, so that the latter is formed in considerable quantity if we take into account the facts that some of the phenyltrimethylammonium iodide is not acted on, and that its molecular weight is very high.

The following products of the reaction were therefore recognised with certainty:—Potassium iodide, dimethylaniline, and trimethylamine; whilst ethane or other hydrocarbon was not identified and cannot have been present in any considerable amount.

If phenyltrimethylammonium were formed and afterwards decomposed, in all probability dimethylaniline and ethane would be produced. The maximum quantity of ethane which could have been formed from 5 grams iodide (13 c.c.) weighs about 0·017 gram, while the amount calculated from the equation—

$$2C_6H_5(CH_3)_3NI + 2K = 2KI + 2C_6H_5N(CH_3)_2 + C_2H_6$$

weighs 0·28 gram, or assuming that one quarter of the iodide remains unchanged 0·21 gram. The formation of trimethylamine also shows that the above equation does not represent the main reaction, and on the whole it appears to us improbable that phenyltrimethylammonium is formed at all.

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LIX.—*The Vapour-density of Hydrofluoric Acid.*

By T. E. Thorpe, F.R.S., and F. J. Hambly.

(Preliminary Notice.)

Gore, in his researches upon anhydrous hydrofluoric acid, showed that by heating a known volume of hydrogen with a slight excess of silver fluoride, the volume of hydrofluoric acid gas formed was approximately twice that of the hydrogen taken, if it were measured at about 100° C., but at lower temperatures it was considerably less than was demanded by the formula HF (*Phil. Trans.*, 1869, 173).

Mallet determined the density of hydrofluoric acid at 30·5° C., by weighing the vapour in a large glass flask coated internally with paraffin, and obtained a value corresponding to the molecular weight 39·32 at that temperature (*Amer. Chem. J.*, 1881, **3**, 189).

Although this result shows that hydrofluoric acid does not give a vapour-density corresponding to the formula HF at temperatures near its boiling point, it cannot be considered as conclusive proof of the existence of the molecule H_2F_2. The alteration in vapour-density may in fact resemble the well-known case of acetic acid, in which there is a gradual and progressive breaking down of a complex molecular grouping. We have, therefore, investigated the subject

with the object of ascertaining whether the gas possesses a constitution corresponding to the formula H_2F_2 through any appreciable range of temperature.

By means of a large platinum apparatus provided with stopcocks of the same metal, we have determined the vapour-density at temperatures varying from 26·4° to 88·3°. Pure anhydrous hydrofluoric acid was prepared as required for each experiment from the acid potassium fluoride and was then redistilled through the platinum apparatus placed in a bath of glycerol and heated to the desired temperature. In all, 14 experiments were made at short intervals of temperature between the points given, and the values obtained correspond to molecular weights ranging from 51·19 at 26·4° to 20·58 at 88·3°, the process of breaking up of the molecular grouping being analogous to that observed in the case of acetic acid.

We hope to be able to lay a detailed account of our experiments before the Society at an early date.

LX.—*Thiophosphoryl Fluoride.*

By T. E. Thorpe, F.R.S., and J. W. Rodger.

(Preliminary Notice.)

When phosphorus pentasulphide is heated with lead fluoride, best in a leaden tube, a gas is formed, which analysis shows to be thiophosphoryl fluoride, PSF_3. Bismuth fluoride heated with phosphorus pentasulphide forms the same gas, but a higher temperature is required to bring about the reaction. We have also been able to prepare the new gas by heating a mixture of sulphur, phosphorus, and fluoride of lead, using a considerable quantity of the last-named substance; the excess serving to moderate the otherwise violent reaction. An additional mode of formation consists in heating a mixture of arsenic trifluoride and thiophosphoryl chloride in a sealed tube at a temperature of 150°; but the most convenient method of preparation, and the one giving the gas in a state of purity, is that first described.

Thiophosphoryl fluoride is a transparent, colourless gas, which may be liquefied in the Cailletet apparatus. In contact with the air, the gas, if pure, spontaneously ignites, burning, if it be issuing from a jet, with a pale, yellowish-green flame, tipped with blue. If the experiment be so arranged that a considerable quantity of the gas is brought in contact with the air, it ignites as before, but produces in

the first instance a beautiful blue flash of light, subsequently followed by the yellowish-green flame easily observed in the case of the jet of gas. Thiophosphoryl fluoride is dissolved by water, but not very rapidly. It has no action on mercury. Under the action of heat or the electric spark it is decomposed with comparative ease, sulphur separating in the first instance. If a quantity of the gas be heated in a glass tube over mercury for some time, the volume alters, phosphorus and sulphur are deposited on the sides of the tube, and the resulting gas consists entirely of silicon tetrafluoride. This reaction may be taken advantage of in order to determine the amount of fluorine in the compound. Observations of its spectrum show that the gas is dissociated at the lowest temperature of the spark. Thiophosphoryl fluoride is soluble to some extent in ether, insoluble in alcohol and benzene. It is completely absorbed by peroxide of lead, and unites with ammonia to form a white solid. Passed over heated sodium, the metal takes fire and burns with a red flame, the residual mass giving off spontaneously inflammable phosphuretted hydrogen on treatment with water.

We reserve the details of our study of the properties of this gas for a communication which we hope to lay before the Society at an early date.

LXI.—*The Action of Bromine on Potassium Ferricyanide.*

By Edgar J. Reynolds, Student in the Laboratory of the Normal School of Science, South Kensington.

In studying the action of the halogens on potassium ferricyanide with the view of obtaining the so-called superferricyanide of potassium, I noticed that a black substance was produced in the later stages of the action. The formation of this was so general, that the reaction seemed to merit further study; it was only observed, however, when the bromine was in excess; when the ferricyanide was in excess, a blue substance was formed very much resembling prussian blue, but apparently it was not homogeneous, and probably contained besides prussian blue, Turnbull's blue and the black substance already mentioned.

It has been known for some time that when chlorine in excess is passed into a solution of potassium ferrocyanide or ferricyanide, and the liquid is heated to boiling, a cyanide of iron generally known by the name of Pelouze's green is formed, and that if the action is con-

tinued, this is converted into a blue compound (generally vaguely described as prussian blue). It is also stated that bromine acts in the same manner as chlorine. With regard to the latter stage of the reaction, namely, the formation of prussian blue, this is correct, as it is also with regard to the first product of the transformation, the so-called superferricyanide of potassium. But with regard to the intermediate stage preceding the formation of the blue compound, the statement is wholly inaccurate, as instead of Pelouze's green we obtain a black, brittle, semicrystalline substance.

In my attempts to obtain the superferricyanide, I used iodine and bromine, these being heated with potassium ferricyanide in sealed tubes at temperatures of 100° and 120° for several hours. With iodine, the products were iodide of cyanogen, potassium iodide, potassium superferricyanide, and prussian (?) blue; with bromine, bromides of cyanogen, potassium bromide, and a much larger quantity of the blue substance were formed, but no trace of potassium superferricyanide could be discovered, the action of the bromine being much more energetic than that of iodine. Blue compounds formed in reactions similar to this are generally vaguely described as prussian blue (as, for example, that formed by the continued action of chlorine on Pelouze's green). As no analyses of such compounds have been made, I prepared a larger quantity by heating the mixture over steam in a flask connected with a reflux condenser, as it was found that the reaction went just as well as in sealed tubes. According to the proportion of bromine used, and the time that the action was allowed to continue, different results were obtained as follows:—

I. When the potassium ferricyanide was in excess, a blue compound was obtained, not unlike Turnbull's blue in properties.

II. When bromine was in excess, and the action was continued for a long time, the blue substance obtained resembled prussian blue rather than Turnbull's blue.

III. When bromine was in excess, and the action was allowed to proceed moderately, and not continued too long, a black substance was formed, as already mentioned, which proved to be a cyanide of iron.

Analyses were made of these three products. The product obtained in reaction I was thrown on to a filter, then treated with dilute hydrochloric acid to free it from any hydrate or oxide of iron which it might contain, and again thoroughly washed, dried at 100°, and analysed. The numbers obtained were as follows:—

0·3137 gram gave 0·2318 gram CO_2 = 20·15 per cent. C.
0·2837 „ 0·1560 „ Fe_2O_3 = 38·49 „ Fe.

This gave the ratio of Fe to C as 1·91 : 1, a proportion somewhat

greater than it would have been had the substance been washed with cold water and dried at the ordinary temperature, as during the drying at 100° there was a slight evolution of hydrocyanic acid. This would not, however, make any great difference, and it was evident that the proportion of iron to carbon in this substance (which seemed homogeneous) was intermediate between that in prussian blue and Turnbull's blue respectively, although nearer the latter.

The product from II was treated in the same manner, except that it was dried at the ordinary temperature. Analysis gave the following results:—

0·3225 gram	gave	0·2401 gram	CO_2	= 20·30	per cent.	C.
0·2506	,,	0·1853	,, CO_2	= 20·16	,,	
0·6028	,,	0·3155	,, Fe_2O_3	= 36·63	,,	Fe.

This gives the ratio of Fe to C as 1·81 : 1, exactly that required for prussian blue, Fe_7Cy_{18}. It was in appearance very like pure prussian blue, although slightly darker, but probably contained also a little unchanged black cyanide of iron, and a small quantity of iron oxide (due to washing with hot water).

Before giving analyses of the product from III, it will be advisable to give a more precise account of its production. It was not obtained in sealed tubes, except when iodine was used, the more energetic action of bromine speedily decomposing it. But when the potassium ferricyanide was heated with bromine in a flask connected with a reflux condenser, the action could be moderated, and a fair yield of this black cyanide obtained. A good proportion to use is 40 grams of bromine to 20 grams of potassium ferricyanide (a saturated solution may be taken), and to maintain the mixture at gentle ebullition for five or six hours. The flask containing the bromine and ferricyanide solution is connected with a reflux condenser, the tube of which is of such a size that it fits accurately into the neck of the flask, because as the action of the bromine has to be continued for a considerable time, nothing in the form of a cork can be made use of. The junction of the tube of the condenser and the neck of the flask may be surrounded with caoutchouc tubing, taking care that they fit sufficiently closely to prevent any of the caoutchouc which may be acted upon by the vapour of the bromine from falling into the flask (a better plan is to seal the inner tube of the condenser on to the neck of the flask).

The substance so formed was treated with dilute hydrochloric acid, thoroughly washed and dried over sulphuric acid in a vacuum. It is advisable to wash with cold water, as although the compound is comparatively stable, hot water seems to separate out a little oxide of iron, and to cause a transformation (though very slowly) into

prussian blue. The separation of oxide of iron would appear from the fact that in testing the filtrate to see whether the washing was sufficiently complete, no trace of iron could be found in it, yet after evaporating some of it to dryness over steam, there was a separation of iron oxide. This could only arise from the water dissolving a small portion of the black substance which was thus decomposed on evaporation; hence the washing with hot water would probably decompose the substance, although only to a very slight extent, so slight that hydrocyanic acid is not always detected. For a similar reason, that is a slight evolution of cyanogen, it should not be dried at an elevated temperature, but over sulphuric acid in a vacuum.

The analyses were made as follows:—The carbon was estimated in the usual manner, and the fixed residue after combustion was dissolved in concentrated hydrochloric acid (with a little nitric acid), and then precipitated by ammonia. In such a compound as this black cyanide, it is highly important that the fixed residue should not be regarded as ferric oxide (as has often been erroneously done), because, as I have pointed out in a previous paper, the error may be considerable, and in this particular case might very nearly amount to the difference between prussian blue and this black cyanide. In these analyses, no estimation has been given of the nitrogen, as it was evident from the method of formation of this substance and its decomposition by potash, that it was a cyanide; but as the analyses of M. J. A. Muller (*Compt. rend.*, **104**, 994) had shown that the group CO occurred in some double cyanides, I afterwards made several nitrogen determinations, which showed that the nitrogen was combined very nearly in the form of cyanogen. It was, however, remarkable that the proportion of nitrogen was always rather too low, but the deficiency was too small to allow of its expression by means of formulæ. The results of the analyses were as follows:—

I.
0·3569 gram gave 0·2458 gram CO_2 = 18·78 per cent. C.
0·3783 „ 0·2608 „ CO_2 = 18·80 „
0·7352 „ 0·3518 „ Fe_2O_3 = 33·50 „ Fe.
0·8278 „ 0·3965 „ Fe_2O_3 = 33·51 „
This gives the ratio of Fe to C as 1·78 : 1.

II.
0·4455 gram gave 0·3379 gram CO_2 = 20·69 per cent. C.
0·8463 „ 0·4323 „ Fe_2O_3 = 35·76 „
This gives the ratio of Fe to C as 1·73 : 1.

III.
0·3973 gram gave 0·3083 gram CO_2 = 21·16 per cent. C.
0·8217 „ 0·4353 „ Fe_2O_3 = 37·08 „ Fe.
1·0627 „ 0·5638 „ Fe_2O_3 = 37·14 „
This gives the ratio of Fe to C as 1·75 : 1.

IV. 0·3415 gram gave 0·2509 gram CO_2 = 20·04 per cent. C.
0·3487 „ 0·2570 „ CO_2 = 20·10 „
0·6902 „ 0·3485 „ Fe_2O_3 = 35·34 „ Fe.
This gives the ratio of Fe to C as 1·76 : 1. It was to all appearance the purest specimen—appearing as a perfectly black powder, even when in the finest state of division.

V. 0·4392 gram gave 0·3351 gram CO_2 = 20·88 per cent. C.
0·8804 „ 0·4500 „ Fe_2O_3 = 35·78 „ Fe.
This gives the ratio of Fe to C as 1·71 : 1.

The mean of the above analyses gives the ratio of Fe to C as 1·75 : 1, which is exactly the proportion required for the formula Fe_3Cy_8. This formula does not include water, as none of the specimens analysed were in comparable states. A specimen, apparently dried as completely as possible over sulphuric acid, gave numbers very nearly corresponding with the formula $Fe_3Cy_8,4H_2O$, thus:—

0·4218 gram gave 0·3338 gram CO_2 = 21·58 per cent. C,
and 0·0738 „ H_2O = 17·49 „ H_2O.
0·4545 gram gave 0·3592 „ CO_2 = 21·55 „ C,
and 0·0736 „ H_2O = 16·19 „ H_2O.

The formula requires 21·43 per cent. C, and 16·07 per cent. H_2O.

Properties and Reactions of the Compound.

Its properties and behaviour with reagents generally resemble those of prussian blue, but it is more stable. It is a semicrystalline powder, hard and brittle, of a jet-black lustre and conchoidal fracture. The change in colour with cyanides of iron with the increase in cyanogen is rather curious, thus we have—

Ferrous cyanide (not isolated), $FeCy_2$, white.
Turnbull's blue, Fe_5Cy_{12}, a fine blue, but not dark.
Prussian blue, Fe_7Cy_{18}, a dark blue.
Black cyanide of iron, Fe_3Cy_8, black.

It is hygroscopic, but not so much so as prussian blue. It is decomposed by potash into ferric hydrate and potassium ferrocyanide and ferricyanide. We should expect that the reaction would be according to the equation—

$$6Fe_3Cy_8 + 30KHO = 5Fe_2(OH)_6 + 3K_8Fe_2Cy_{12} + K_6Fe_2Cy_{12},$$

but the proportion of ferric hydrate separated is rather greater than this equation shows. Thus from a sample of the product from (II) when simply decomposed by potash without heating, 19·76 per cent. Fe

separated; when boiled with potash, 20·70 per cent. Fe separated, out of a total of 33·51 per cent. Fe. This greater proportion might arise from some having been already separated, and partly from the ferricyanide formed being further decomposed, which, according to Skraup, takes place in accordance with the equation—

$$3Fe_2Cy_{12}K_6 + 10KOH = 2Fe_2Cy_{12}K_3 + Fe_2(OH)_6 + 10CyK + 2CyOK + 2H_2O.$$

The decomposition by potash was precisely similar to that observed by Williamson on the green compound obtained by him by the continued action of oxidising agents on the ferricyanide of iron and potassium, namely, first a separation of ferric hydrate and a brown liquid (containing potassium ferrocyanide and ferricyanide), which on boiling further deposited ferric hydrate. Hence the discrepancy in the two results given above (1 per cent.).

After long-continued digestion, concentrated hydrochloric acid dissolves it completely, yielding a mixture of ferrous and ferric chlorides. Even the strongest nitric acid has very little effect, but when digested with it for a long time it gradually decomposes it by oxidation. On the addition of cold, concentrated sulphuric acid it is converted into a white, pasty mass, which would appear to be the same product as that formed when prussian blue is treated in a similar way, for when water is added to this a blue substance is formed. When boiled with excess of strong sulphuric acid, it dissolves entirely, but a blue substauce is precipitated on adding water.

Chlorine and bromine gradually decompose it, yielding prussian blue.

By the prolonged action of the air, its colour changes to a dull blue, the substance being apparently transformed into prussian blue. It may at first seem anomalous that both this black cyanide and Turnbull's blue should be transformed on exposure to the air into prussian blue, which is intermediate in composition between the two. But whereas in the latter case it is a process of oxidation, in the former it appears to be due to the presence of moisture, as if kept in a dry place it remains unchanged for a very long time. The reaction is probably as follows:—

$$3Fe_2Cy_6 + 6H_2O = Fe_2(OH)_6 + Fe_7Cy_{18}\text{ (prussian blue)} + 6HCy,$$

whereas, in the case of Turnbull's blue, it is—

$$6Fe_2Cy_{12} + 3O = 4Fe_7Cy_{18} + Fe_2O_3.$$

When heated it gives off cyanogen, and in presence of moisture

hydrocyanic acid and ammonia, forming ammonium cyanide. When heated more strongly in air, it burns and leaves oxide of iron.

Is this compound to be regarded as ferrosoferric ferricyanide, $Fe''_3Fe'''_2(Fe_2Cy_{12})_2$, or as a cyanide of iron similar to the magnetic oxide, viz., $Fe_2Cl_6,FeCl_3$? The method of its formation does not afford us much assistance in answering this question, as it consists essentially in the abstraction of potassium by the bromine. The whole molecule of the potassium ferricyanide is split up, ferric bromide is formed, which acting on the undecomposed ferricyanide might give ferric cyanide, $FeCy_3$. But the Fe atom would seem under ordinary conditions incapable of holding three cyanogen-atoms, and hence is immediately decomposed into a stable cyanide (apparently the most stable of the cyanides of iron), namely, Fe_3Cy_8. Wyrouboff does indeed claim to have obtained the compound $FeCy_3$, but has not published his analyses; and he gives the following equation to explain the reaction: — $2Cy_6FeK_4 + 8NH_4Cl + Aq = 6CyNH_4 + Cy_6Fe_2,3H_2O + 8KCl + 2NH_4$ (*Ann. Chem. Phys.*, **47**, 16, 284), in which NH_4 stands by itself, which is absurd. Endeavours to obtain this ferric cyanide, $FeCy_3$, were not successful. Attempts to determine whether the view taken above of the method of formation of the black cyanide was correct (namely, the action of bromine on ferricyanide) did not meet with success. The plan adopted was by acting with bromine on the substance produced by the action of ferric chloride in excess on potassium ferricyanide. Prussian blue was formed after some time, but at no stage could the formation of the black cyanide be observed.

The nature of the decomposition of the black cyanide by potash strongly favours the view that it is a ferrosoferric ferricyanide. This same view is also supported by the results of some analyses I made of the compound before I was aware that potassium was not one of its constituents. Thus one analysis showed 6·59 per cent. K, 34·16 per cent. Fe, and 22·83 per cent. C. Here, by adding to the iron found the amount of ferrous iron equivalent to the potassium, we get the ratio of Fe : C as already found, that is, 1·75 : 1; and it would thus seem to indicate that the displacement of potassium by ferrous iron (Fe″) takes place in the later stages of the reaction, which is precisely what we should expect.

LXII.—*Some Amines and Amides derived from the Nitranilines.*

By Raphael Meldola, F.R.S., and E. H. R. Salmon.

In the course of a series of investigations on diazoamido-compounds, by one of the authors and Mr. F. W. Streatfeild, the results of which have been made known to the Chemical Society in former papers, the occasion has arisen for preparing a number of new or imperfectly known alkyl-derivatives of the nitranilines, and it appeared of sufficient interest to collect together all our results, and to place them on record as a contribution towards the knowledge of substituted ammonias. The question as to whether there can exist more than one modification of a secondary or tertiary amine or amide has been approached by previous investigators, and since the problem was first attacked by Hofmann in 1850 (*Annalen*, **74**, 168), evidence of such isomerism has been obtained by Lossen in his well-known investigations on the derivatives of hydroxylamine (*Annalen*, **175**, 275; *ibid.*, 327; **181**, 388; **182**, 220; **186**, 45; *Ber.*, 1877, 2223). With respect to the amides derived from aniline, the only known case of isomerism is that of dibenzoylanilide, which has been obtained in two modifications, one (m. p. 136°) obtained by the action of benzoyl chloride on benzanilide (Gerhardt and Chiozza, *Compt. rend.*, **37**, 90), and the other (m. p. 150°) by heating phenylthiocarbimide with benzoic acid (Losanitch, *Ber.*, 1873, 176). These results were confirmed by Higgin in a paper published by the Society in 1882 (Trans., 1882, 132). A study of the amines and amides derived from aromatic monamines by the substitution of various radicles for the amidic hydrogen is, therefore, of interest in connection with the general question of chemical isomerism, and although we have at present no new evidence on this subject to bring forward, the results recorded in the present paper will furnish materials upon which it is hoped to base a further series of experiments having for their object the discovery of new cases of isomerism of the kind indicated.

The alkyl-nitranilines can be readily prepared in a state of purity by decomposing the alkyl-derivatives of the corresponding diazoamido-compounds by means of hydrochloric acid (Meldola and Streatfeild, Trans., 1887, 108). It is only necessary to alkylate the dinitrodiazoamido-compound by cohobation with alcoholic potash and the iodide or bromide of the alkyl radicle in the usual way, and then to heat the alkyldiazoamido-derivative with strong hydrochloric acid till decomposition is complete :—

$$NO_2{\cdot}C_6H_4{\cdot}N_2(R'){\cdot}C_6H_4{\cdot}NO_2 + HCl = NO_2{\cdot}C_6H_4{\cdot}Cl + NO_2{\cdot}C_6H_4{\cdot}NHR' + N_2.$$

The acid solution is steam distilled to get rid of the nitrochlorbenzene, and after filtration to remove tarry impurities, the alkylnitraniline is thrown out by alkali. This method offers many advantages over the ordinary process of direct alkylation of the nitranilines in the presence of caustic alkali, as the alkyl-derivative has always to undergo purification in the older method by conversion into the nitrosamine, and the decomposition of the latter by cohobation with alcoholic hydrochloric acid is a very lengthened operation.

1. *Methyl-paranitraniline.*

This compound was prepared by the decomposition of the methyl-derivative of paradinitrodiazoamidobenzene,

$$(p)NO_2{\cdot}C_6H_4{\cdot}N_2(CH_3){\cdot}C_6H_4{\cdot}NO_2(p),$$

(m. p. 219°; Trans., 1888, 666), by hydrochloric acid in the manner above described. After crystallisation from alcohol, the methylnitraniline forms thick, stumpy prisms of a yellowish-brown colour. If allowed to crystallise rapidly from dilute alcohol, it separates in the form of small, square tablets, which under the microscope appear yellow by transmitted light, and violet by reflected light. The pure substance melts at 152°. It possesses slight basic properties, being dissolved by strong hydrochloric acid, but the solution becomes yellow, and the free base is precipitated on diluting with water. A determination of nitrogen gave the following results:—

0·0518 gram, burnt in a vacuum with CuO, gave 8 c.c. moist N at 10·5° and 757 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_3$.	Found.
N	18·42	18·37

The base is slightly soluble in hot water; readily soluble in alcohol and the benzene hydrocarbons. It separates from its aqueous solution on cooling in the form of yellow scales.

Paranitrophenyl-methylnitrosamine, $(p)NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}NO$.

This compound separates as an ochreous, flocculent precipitate on adding sodium nitrite to a solution of methyl-paranitraniline in hydrochloric acid. After crystallisation from dilute alcohol it was obtained in the form of straw-coloured needles, and was finally purified by crystallisation from a mixture of benzene and petroleum,

the pure substance forming hard and thick, ochreous scales, melting at 100°.

0·1542 gram, burnt in a vacuum with CuO, gave 30·4 c.c. moist N at 15·5° and 754 mm. bar.

	Calculated for $C_7H_7N_3O_3$.	Found.
N	23·20	22·84

Methylacetyl-paranitranilide, $(p)NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}C_2H_3O$.

Methyl-paranitraniline was boiled for about half an hour with acetic anhydride and a little anhydrous sodium acetate. The product was washed with cold water, and then dissolved in boiling water, the solution on cooling depositing the acetyl-derivative in the form of rosettes of fern-like leaflets of a yellowish-white colour. The melting point is 153°. When allowed to crystallise slowly from a somewhat dilute aqueous solution, the substance forms long, straw-coloured, slender needles.

The following results were obtained on analysis:—

0·1362 gram gave 0·2764 gram CO_2 and 0·0626 gram H_2O.

0·1034 gram, burnt in a vacuum with CuO, gave 13·2 c.c. moist N at 17·5° and 755 mm. bar.

	Calculated for $C_9H_{10}N_2O_3$.	Found.
C	55·67	55·34
H	5·15	5·10
N	14·43	14·67

The acetyl-derivative above described having been prepared by the acetylation of methyl-paranitraniline, an attempt was made to prepare the same, or an isomeric substance, by the methylation of acetyl-paranitranilide. For this purpose the latter compound was suspended in absolute alcohol in which the theoretical quantity of sodium had been previously dissolved, and the necessary quantity of methyl iodide added. The mixture was heated in a flask with reversed condenser for some time, and on examining the product it was found that the sodium ethylate had simply removed the acetyl-group, the resulting compound being paranitraniline.

Methylbenzoyl-paranitranilide, $(p)NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}C_7H_5O$.

This compound is easily prepared by heating methyl-paranitraniline for about half an hour with benzoyl chloride or with benzoic anhydride. The product, after being washed with warm dilute

ammonia till free from benzoic acid, was crystallised from dilute alcohol, and thus obtained in the form of thick, brown prisms melting at 111—112°.

0·1480 gram, burnt with CuO in a vacuum, gave 13·6 c.c. N at 19° and 770·7 mm. bar.

	Calculated for $C_{14}H_{12}N_2O_3$.	Found.
N	10·94	10·71

The substance is slightly soluble in boiling water, the solution depositing whitish, glistening rhombohedra on cooling. This benzoyl-derivative is no doubt identical with that obtained by Hess by the nitration of benzoyl-monomethylaniline (*Ber.*, 1885, 686).

Attempts have been made to introduce two acid radicles into para-nitraniline, but hitherto without success. In the first place benzoyl-paranitranilide was prepared by the action of benzoyl chloride on paranitraniline. The pure compound had the melting point 199° ascribed to it by Hübner (*Annalen*, **208**, 292). After boiling for about two hours with acetic anhydride and dry sodium acetate the substance was found to be unacetylated. In the next place acetyl-paranitranilide was heated with benzoyl chloride in order to ascertain whether acetylbenzoyl-paranitranilide could be prepared by this means, but the resulting product was found to be benzoyl-paranitranilide, the benzoyl simply displacing the acetyl-group.

2. *Methyl-metanitraniline.*

This substance was prepared both by the decomposition of the methyl-derivative of metadinitrodiazoamido-benzene (m. p. 127—128°, Trans., 1888, 667), as well as by the action of methyl iodide on meta-nitraniline in the presence of caustic soda (Nölting and Stricker, *Ber.*, 1886, 548). The products were identical and were utilised for the preparation of the following derivatives:—

Methylacetyl-metanitranilide, $(m)NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}C_2H_3O$.

Methyl-metanitraniline was acetylated by means of acetic anhydride in the usual way, and the product crystallised from boiling water. It separates on cooling in the form of stellate tufts of thick, whitish needles melting at 94—95°.

0·1132 gram, burnt in a vacuum with CuO, gave 13·9 c.c. N at 17° and 761·4 mm. bar.

	Calculated for $C_9H_{10}N_2O_3$.	Found.
N	14·43	14·17

Methylbenzoyl-metanitranilide, $(m)NO_2 \cdot C_6H_4 \cdot N(CH_3) \cdot C_7H_5O$.

Prepared by the action of benzoyl chloride on methyl-metanitraniline. The substance is soluble in boiling water, from which it separates on cooling in beautiful, iridescent scales, which become silvery-white on drying. The melting point is 104—105°.

0·1506 gram, burnt in a vacuum with CuO, gave 14·6 c.c. N at 15° and 763·2 mm. bar.

	Calculated for $C_{14}H_{12}N_2O_3$.	Found.
N	10·94	11·39

An attempt was made to methylate acetyl-metanitranilide by the action of sodium ethylate and methyl iodide in the usual way, but the acetyl-group was simply eliminated and metanitraniline left With reference to the melting point of acetyl-metanitranilide some discrepancy exists, Meyer and Stüber giving 141—143° (*Annalen*, **165**, 183), and Kleeman 141° (*Ber.*, 1886, 337). Our preparation was obtained by the action of acetic anhydride on metanitraniline, and after purification by crystallisation from boiling water formed white, stumpy rhomboidal prisms melting at 150—150·5°.

3. *Ethylnitranilines.*

Ethyl-paranitraniline was prepared by the decomposition of the corresponding ethylated diazoamido-compound, as well as by the action of ethyl bromide on paranitraniline in the presence of caustic potash according to the method of Schweitzer (*Ber.*, 1886, 149). The nitrosamine (m. p. 119·5°) has been described in a former paper (Meldola and Streatfeild, Trans., 1886, 631).

Ethylacetyl-paranitranilide, $(p)NO_2 \cdot C_6H_4 \cdot N(C_2H_5) \cdot C_2H_3O$.

Prepared by the action of acetic anhydride and dry sodium acetate on ethyl-paranitraniline. After crystallisation from boiling water, the substance forms flat, white needles fusing at 118—119°.

0·1240 gram gave 0·2608 gram CO_2 and 0·0628 gram H_2O.

0·1450 gram, burnt in a vacuum with CuO, gave 16·8 c.c. moist N at 20° and 754·7 mm. bar.

	Calculated for $C_{10}H_{12}N_2O_3$.	Found.
C	57·69	57·36
H	5·76	5·62
N	13·46	13·15

The substance is no doubt identical with that obtained by Weller by the nitration of ethylacetanilide (*Ber.*, 1883, 31).

Ethylbenzoyl-paranitranilide, $(p)NO_2 \cdot C_6H_4 \cdot N(C_2H_5) \cdot C_7H_5O$.

Obtained by the action of benzoyl chloride on ethyl-paranitraniline in the usual way. The substance was purified by crystallisation from dilute alcohol, and was obtained in the form of bundles of flat, white needles from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch in length. The melting point is 98°. The substance is almost insoluble in hot water, but readily soluble in alcohol.

0·2006 gram, burnt in a vacuum with CuO, gave 18·2 c.c. moist N at 23° C. and 758·5 mm. bar.

	Calculated for $C_{15}H_{14}N_2O_3$.	Found.
N	10·37	10·20

The acetyl-derivative of ethyl-metanitraniline prepared by direct acetylation fuses at 88—89° (Nölting and Stricker, *Ber.*, 1886, 550). The corresponding benzoyl-derivative is a viscid oil which does not solidify on standing at ordinary temperatures.

4. *Benzylnitranilines.*

Benzyl-paranitraniline (m. p. 142—143°), obtained by the decomposition of benzylated paradinitrodiazoamidobenzene, has been described with its nitrosamine in a previous paper (Trans., 1887, 113). A simpler method of preparing this compound is the following:—

Paranitraniline is mixed with the theoretical quantity of benzyl chloride and excess of a strong solution of caustic soda added to the contents of the flask. The mixture is kept near the boiling point for about 48 hours, the loss of benzyl chloride being prevented by using a reversed condenser. When the benzylation is complete, steam is blown through the contents of the flask to remove any excess of benzyl chloride, and the product is collected, washed with water, and then boiled with dilute hydrochloric acid in order to dissolve out any unaltered nitraniline. The crude benzyl-paranitraniline can be purified by crystallisation from glacial acetic acid or from alcohol.

Benzylacetyl-paranitranilide, $(p)NO_2 \cdot C_6H_4 \cdot N(C_7H_7) \cdot C_2H_3O$.

Prepared by the action of acetic anhydride and dry sodium acetate on the benzyl-derivative. By crystallisation from dilute alcohol the substance was obtained pure in the form of yellowish, rhombohedral crystals fusing at 108—109°.

0·1800 gram, burnt in a vacuum with CuO, gave 16·2 c.c. moist N at 20° and 748·8 mm. bar.

	Calculated for $C_{15}H_{14}N_2O_3$.	Found.
N	10·37	10·13

Benzylbenzoyl-paranitranilide, $(p)NO_2 \cdot C_6H_4 \cdot N(C_7H_7) \cdot C_7H_5O$.

Prepared by the action of benzoyl chloride on benzyl-paranitraniline. Crystallised from dilute alcohol it forms long, flat, whitish needles melting at 194°.

0·1326 gram, burnt in a vacuum with CuO, gave 9·6 c.c. moist N at 19° C. and 762·2 mm. bar.

	Calculated for $C_{20}H_{16}N_2O_3$.	Found.
N	8·43	8·34

Benzyl-metanitraniline (m. p. 107°; Trans., 1887, 114) was prepared by the same method as the para-derivative. Both the acetyl- and benzoyl-derivatives are viscid oils which do not solidify on standing at ordinary temperatures.

In the course of the foregoing investigation a few comparative experiments have been made with unsubstituted anilides:—

5. *Action of Benzoyl Chloride on Acetanilide.*

The substances were heated together as long as hydrochloric acid was evolved. The product was then washed with water, and boiled with dilute ammonia till the benzoic acid was removed. The residue after crystallisation from dilute alcohol formed small, white scales melting at 161°, and having all the properties of benzanilide:—

0·1130 gram gave 0·3270 gram CO_2 and 0·0546 gram H_2O.

	Calculated for $C_6H_5 \cdot NH \cdot C_7H_5O$.	Found.
C	79·19	78·92
H	5·58	5·36

The action of benzoyl chloride is thus simply to replace acetyl by benzoyl. The same result was obtained with benzoic anhydride.

On the other hand, benzanilide was boiled with acetic anhydride and dry sodium acetate for two or three hours, at the end of which time the product was examined and found to be unaltered benzanilide, no acetylation having taken place.

Benzylacetanilide is easily prepared by the acetylation of benzylaniline with acetic anhydride; at ordinary temperatures it is a thick, oily liquid.

Finsbury Technical College,
July 16th, 1888.

LXIII.—*The Rotatory Power of Benzene-derivatives.*

By J. Lewkowitsch, Ph.D.

The concluding remarks in the paper of F. Herrmann (*Berichte*, **21**, 1959) refer to a subject on which I have been making a few experiments. In one of my papers (*ibid.*, **16**, 1576) I mentioned that, if benzene be represented by Ladenburg's prism symbol, an asymmetric carbon-atom may be contained in a tri-derivative in which there are three dissimilar radicles, the position of which, represented by means of the conventional simple hexagon symbol, are 1 : 2 : 3, the asymmetric carbon-atom being that in the position 5.

Although it is very unlikely indeed that such substances would be possessed of rotatory power, it is conceivable that they might be resolved into two substances of opposite rotatory power, just as I succeeded in splitting mandelic acid into two optically active isomerides (*ibid.*, **16**, 2721).

Through the kindness of Professor O. Jacobsen I was enabled to examine four benzene-derivatives which seemed to be suitable for my purpose, viz.:—

β-Metahomosalicylic acid, $C_6H_3(\overset{1}{C}H_3)(\overset{2}{C}OOH)(\overset{3}{O}H)$.*

β-Orthohomometahydroxybenzoic acid, $C_6H_3(\overset{1}{O}H)(\overset{2}{C}H_3)(\overset{3}{C}OOH$ *

Methoxytolnic acid, $C_6H_3(\overset{1}{O}CH_3)(\overset{2}{C}H_3)(\overset{3}{C}OOH)$.†

α-Nitro-orthotoluic acid, $C_6H_3(\overset{1}{N}O_2)(\overset{2}{C}H_3)(\overset{3}{C}OOH)$.‡

When examined by the polariscope, they did not exhibit any rotatory power. I tried to split the first three by converting them into their cinchonine salts (comp. malic acid, mandelic acid). The cinchonine salts crystallised very well indeed, but the acids thrown down by ammonia from their solutions were optically inactive. The method of splitting by allowing fungi to grow in a solution containing the substances to be examined could only be tried with the fourth substance, as mere inspection of the formulæ would indicate; but even this substance has such strong antiseptic properties that *Penicillium glaucum* did not thrive in its solution.

* *Ber.*, **16**, 1963. † *ibid.*, **16**, 1964. ‡ *ibid.*, **16**, 1958.

LXIV.—*The Solubility of Isomeric Organic Compounds and of Mixtures of Sodium and Potassium Nitrates, and the Relation of Solubility to Fusibility.*

By Thos. Carnelley, D.Sc., and Andrew Thomson, D.Sc., M.A.,
University College, Dundee.

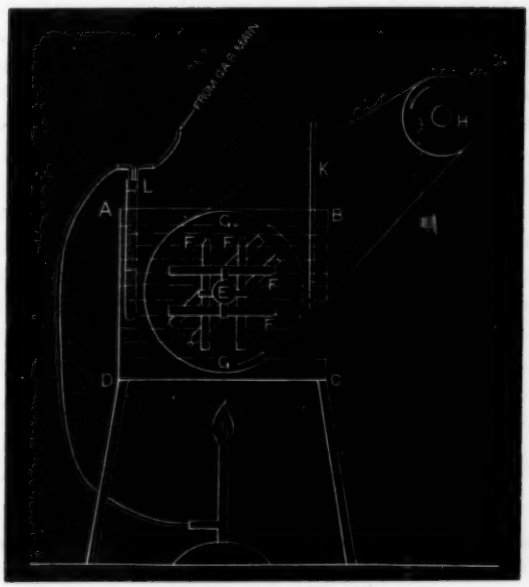
Nearly seven years ago (1881) one of us showed in an opening address given to the Owens College Chemical Society, and subsequently published in the *Philosophical Magazine* [5], **13**, 180, that solubility and fusibility were very closely related to one another, so that of two or more isomeric bodies, that dissolves the most easily which has the lowest melting point, and in which the atomic arrangement is the least symmetrical. Very shortly after Dr. Tilden, in a paper in the *Philosophical Transactions*, 1884, Part I, p. 23, also this Journal, **45**, 266, proved that there was a similar connection between the solubility and fusibility of inorganic compounds.

At that time the investigation had included only a comparatively small number (58) of compounds taken at random from *Watts's Dictionary of Chemistry*, and involved no original experiments made with special reference to the subject. We have now extended the investigation so as to include all isomeric sets of carbon compounds whatever. Our data have been obtained partly from literature and partly as the results of our own determinations.

Before giving the results of our work it will be necessary to describe the method we have employed for the estimation of the solubilities of any set of isomeric organic compounds, and for the other cases referred to in the present paper. For this purpose it was absolutely necessary that for each set of isomerides the determinations should be carried out under identically the same conditions, and to attain this we have in all cases made the determinations for the several members of a set of isomerides simultaneously. The results, however, are not only strictly comparable, but are likewise as absolutely correct as we could make them.

A set of long (110 mm.) and narrow (14 mm. outside diameter) glass phials, accurately stoppered, were employed to hold the solvent and various isomerides under investigation. These bottles were about two-thirds filled with the solvent, and such a quantity of each of the isomerides respectively as would be more than sufficient to form a saturated solution at a temperature 10° above that at which the solubility was to be determined. The stoppers were then firmly inserted and the bottles fixed in suitable clips attached to an axis

passing through the centre of a bath filled with water, and so arranged that the phials were completely immersed. The axis could be kept in regular rotation any length of time by means of a small water motor, whilst the bath was maintained at a constant temperature by a thermo-regulator. The following sketch will represent the arrangement. ABCD is a bath made of tin-plate and standing on a tripod. To the axis E are soldered six brass clips, by means of which as many bottles may be fixed on the axis at the same time. FF represents six such phials, containing the solvent and substances under investigation. Six determinations could thus be made simultaneously. GG and H is a pair of pulleys connected by a cord, H being fixed on



About ⅓th the actual size.

the axis of the small water-motor for driving the apparatus. L is the thermo-regulator to be used in connection with the lamp for heating the bath, and K the thermometer for indicating the temperature. All our determinations, contained in the present paper, were made at 20° C. In order, therefore, to obtain thoroughly saturated solutions the bath was heated to about 30°, and the phials kept immersed and in continual motion for about two hours, matters being so arranged that some at least of the compounds remained still undissolved at 30°, in order to avoid supersaturation. At the end of that time the lamp was turned out and the bath allowed to cool down

to exactly 20° C., the phials being kept in continual motion throughout. This usually took about two hours. After standing for a few minutes so as to allow the still undissolved portions to settle to the bottom of the phials, a quantity of the saturated liquid from each was withdrawn into a small tared glass bottle and weighed. This gave the weight of the solvent and substance dissolved. To determine the quantity of the latter, the solution was evaporated to dryness and the residue weighed. If, however, the substance was volatile when evaporated, this method could not be employed, and in some cases very great difficulty has been experienced in making an exact determination. But when the compound was coloured, the quantity in solution could be easily estimated colorimetrically by titrating it against a standard solution of the same substance in the same solvent. In the case of acids or alkalis also, the amount could be determined by means of a standard acid or alkali, certain modifications, however, being necessary in the presence of some of the solvents. The difference between the total weight of the solution and that of the substance dissolved gave the weight of the solvent which had been required to dissolve that weight of substance at the given temperature. By the above method results are obtained which are strictly comparable, because each set of isomerides can be worked simultaneously, whilst complete saturation is ensured and supersaturation avoided. Special tests made for the purpose showed that the phials were thoroughly tight at the stoppers, even when such a volatile solvent as ether was employed. Altogether we have found the arrangement to answer admirably.

I. (*a.*) *Determination of the Solubilities of* 1 : 3 *and* 1 : 4 *Nitranilines* (m. p. 114° and 147°).

The quantity of these compounds dissolved by a given solvent could not be determined by evaporating a weighed quantity of the saturated solution to dryness on the water-bath, as both of them were slightly volatile under these circumstances. Thus, 0·7015 gram of the 1·3 compound, after solution in water and evaporation to dryness, weighed only 0·6280 gram, or had lost nearly 15·0 per cent. in weight, while the 1·4-compound, though not nearly so volatile, still suffered a perceptible loss. Therefore, as both meta- and para-nitraniline form coloured solutions, the quantity of these compounds, dissolved by a given solvent, was estimated colorimetrically by titration against a standard solution of the nitraniline in the solvent under investigation. That this method gives good results was shown by the following test determinations of the nitraniline dissolved in solutions containing known quantities:—

		Weight of nitraniline taken.	Weight found by experiment.
Experiment	I.....	0·0162 gram	0·0165 gram.
„	II.....	0·0030 „	0·0029 „
„	III.....	0·0075 „	0·0075 „
„	IV.....	0·0099 „	0·0100 „

As the colour of the solution pales somewhat when kept for more than a day, especially on exposure to light, it is necessary that the determinations should be made as soon as possible, and that the standards should be freshly prepared.

By the above method we have determined the solubility of the meta- and para-nitranilines in 13 different solvents, with the results given in Table I, p. 786. All the determinations refer to 20° C. Column I gives the solvent; Column II the modification of nitraniline referred to; Column III the number of the experiment, each of which is the result of an entirely independent determination. The determinations in a given solvent, to which the same number is attached, were always made simultaneously, and in all respects under the same conditions. Column IV gives the weight of the solution taken saturated at 20° C; Column V the strength of the standard employed; Column VI the number of c.c. of this standard required to produce a colour in 50 c.c. of the solvent, equal to that of the weight of liquid in Column IV, also made up to 50 c.c.; Column VII the solubility represented in parts by weight dissolved in 100 parts by weight of the solvent; and Column VIII the mean of the results in Column VII.

(*b.*) *Determination of the Solubility of Mixtures of Sodium and Potassium Nitrates in Water.*

The results were obtained with the apparatus above described, and in the manner already detailed, except that the mixed salts were exposed to the action of the solvent for four instead of two hours. Those experiments to which the same number is attached were made simultaneously. (See Table II, p. 789.)

The composition of the dissolved portion of the mixed salts was ascertained:—(*a.*) By finding the weight of mixed sulphates obtained from a known weight of the mixed nitrate residue left on evaporating the several saturated solutions to dryness; (*b.*) By determining the melting and solidifying points of the several mixed nitrate residues. Reference to the curves in Diagram I then gave the composition corresponding to a given melting or solidifying point.

The melting and solidifying points of the original mixtures *before* solution, and of the dissolved portion *after* solution and evaporation,

TABLE I.

I. Solvent.	II. Substance:—Nitraniline.	III. No. of experiment.	IV. Weight of solution taken, saturated at 20° C.	V. 1 c.c. of standard solution contained of nitraniline.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
				gram.			
Water, H_2O	meta	1	4·839	0·00081	7·2	0·120	0·114
	,,	2	4·716	0·00068	8·1	0·112	
	,,	3	3·605	0·00098	4·3	0·117	
	,,	4	5·022	0·00098	5·6	0·109	
	para	1	4·859	0·00080	4·7	0·078	0·077
	,,	2	4·870	0·00114	3·2	0·075	
	,,	3	4·521	0·00062	5·5	0·076	
	,,	4	4·959	0·00062	6·3	0·079	
Methyl alcohol, $CH_3{\cdot}OH$..	meta	1	2·592	0·02208	11·9	11·28	11·06
	,,	2	2·412	0·01585	14·9	10·85	
	para	1	2·522	0·02789	8·0	9·70	9·59
	,,	2	2·069	0·01338	13·4	9·48	
Ethyl alcohol, $C_2H_5{\cdot}OH$ ..	meta	1	2·393	0·02208	7·1	7·01	7·05
	,,	2	2·565	,,	7·8	7·15	
	,,	3	2·595	,,	7·6	6·99	
	para	1	3·929	0·02789	7·6	5·70	5·84
	,,	2	2·540	,,	5·0	5·81	
	,,	3	2·388	,,	5·0	6·02	
Propyl alcohol, $C_3H_7{\cdot}OH$..	meta	1	2·472	0·02053	6·3	5·52	5·65
	,,	2	2·662	,,	7·1	5·79	
	para	1	2·795	0·01391	8·8	4·58	4·35
	,,	2	2·840	,,	8·1	4·13	

TABLE I—*continued.*

I. Solvent.	II. Substance :— Nitraniline.	III. No. of experiment.	IV. Weight of solution taken, saturated at 20° C.	V. 1 c.c. of standard solution contained of nitraniline.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
				gram.			
Isobutyl alcohol, $C_4H_9 \cdot OH$.	meta	1	2·685	0·02000	3·4	2·60	2·64
	,,	2	2·378	,,	3·1	2·68	
	para	1	2·414	0·01356	3·3	1·89	1·91
	,,	2	2·288	,,	3·2	1·94	
Isoamyl alcohol, $C_5H_{11} \cdot OH$	meta	1	3·399	0·02208	12·0	8·46	8·51
	,,	2	2·715	,,	9·7	8·56	
	para	1	3·059	0·02789	6·4	6·19	6·29
	,,	2	2·680	,,	5·8	6·39	
Ethyl Ether $(C_2H_5)_2O$	meta	1	2·426	0·01587	11·2	7·91	7·89
	,,	2	2·606	,,	12·0	7·88	
	para	1	2·930	0·01278	12·9	5·96	6·10
	,,	2	2·365	,,	10·9	6·25	
Benzene, C_6H_6	meta	1	2·705	0·01576	4·3	2·57	2·45
	,,	2	3·726	,,	5·4	2·34	
	para	1	2·413	0·00698	7·2	2·13	1·98
	,,	2	3·700	,,	9·5	1·83	
Toluene, C_7H_8	meta	1	3·052	0·01576	3·2	1·68	1·71
	,,	2	3·212	,,	3·5	1·75	
	para	1	2·962	0·00698	5·6	1·34	1·31
	,,	2	3·417	,,	6·2	1·29	

TABLE I—*continued.*

I. Solvent.	II. Substance:—Nitraniline.	III. No. of experiment.	IV. Weight of solution taken, saturated at 20° C.	V. 1 c.c. of standard solution contained of nitraniline.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
				gram.			
Cumene, C_9H_{12}	meta	1	3·119	0·01660	2·2	1·18	1·15
	,,	2	3·086	,,	2·1	1·11	
	para	1	3·520	0·01158	2·8	0·93	0·90
	,,	2	3·120	,,	2·3	0·86	
Chloroform, $CHCl_3$.....	meta	1	5·487	0·01660	9·9	3·09	3·01
	,,	2	3·846	,,	6·6	2·94	
	para	1	4·329	0·01158	8·0	2·42	2·31
	,,	2	4·790	,,	8·9	2·20	
Carbon tetrachloride, CCl_4.	meta	1	5·178	0·01660	0·65	0·21	0·21
	,,	2	5·992	,,	0·80	0·22	
	para	1	4·878	0·01158	0·70	0·17	0·17
	,,	2	3·450	,,	0·55	0·18	
Carbon disulphide, CS_2....	meta	1	4·854	0·01660	0·95	0·33	0·33
	,,	2	5·138	,,	1·05	0·34	
	para	1	2·906	0·01158	0·65	0·26	0·26
	,,	2	3·416	,,	0·80	0·27	

TABLE II.

I. No. of experiment.	II. Composition of mixed salts submitted to the action of the solvent.	III. Weight of solution taken saturated at 20°.	IV. Weight of residue obtained.	V. Solubility. Parts by weight of mixed salts in 100 parts of water.	VI. Mean solubility at 20°.
1	100 p. c. $NaNO_3$	5·036	2·372	89·04	86·8
4	„ „	6·614	3·087	84·7	
1	90 p. c. $NaNO_3$ + 10 p. c. KNO_3	4·509	2·339	107·9	109·6
2	„ „ „	4·807	2·537	111·4	
1	80 p. c. $NaNO_3$ + 20 p. c. KNO_3	4·407	2·523	133·9	136·5
3	„ „ „	9·6005	5·566	138·0	
4	„ „ „	8·083	4·629	134·0	
5	„ „ „	5·778	3·352	138·1	
1	70 p. c. $NaNO_3$ + 30 p. c. KNO_3	4·543	2·574	130·7	136·3
3	„ „ „	6·019	3·5095	139·8	
4	„ „ „	3·351	1·939	136·7	
5	„ „ „	2·817	1·635	138·3	
1	60 p. c. $NaNO_3$ + 40 p. c. KNO_3	4·978	2·868	135·4	137·6
3	„ „ „	5·573	3·268	141·7	
4	„ „ „	4·354	2·530	138·7	
1	50 p. c. $NaNO_3$ + 50 p. c. KNO_3	3·898	2·001	105·4	106·1
2	„ „ „	4·364	2·254	106·9	
1	45·7 p. c. $NaNO_3$ + 54·3 p.c. KNO_3 = molecular proportions	5·727	2·669	87·2	88·0
2	„ „ „	4·167	1·959	88·7	

TABLE II—*continued.*

I. No. of experiment.	II. Composition of mixed salts submitted to the action of the solvent.	III. Weight of solution taken saturated at 20°.	IV. Weight of residue obtained.	V. Solubility. Parts by weight of mixed salts in 100 parts of water.	VI. Mean solubility at 20°.
1	40 p. c. $NaNO_3$ + 60 p.c. KNO_3	4·761	2·159	82·9	81·1
2	„ „ „	3·614	1·594	79·3	
1	30 p. c. $NaNO_3$ + 70 p. c. KNO_3	3·837	1·643	74·9	73·5
2	„ „ „	5·663	2·368	72·1	
1	20 p. c. $NaNO_3$ + 80 p. c. KNO_3	4·102	1·429	53·4	54·1
2	„ „ „	4·149	1·469	54·8	
1	10 p. c. $NaNO_3$ + 90 p. c. KNO_3	5·189	1·534	41·9	40·9
2	„ „ „	4·456	1·263	39·9	
1	100 p. c. KNO_3	2·626	0·668	34·1	33·6
2	„	3·466	0·864	33·2	

were determined in the ordinary way by heating small quantities of the substance in somewhat large capillary glass tubes, attached to a thermometer immersed in a bath of strong sulphuric acid. In the case of the pure nitrates, for which an ordinary thermometer cannot well be used, the specific heat method formerly described (this Journal, **29**, 489) by one of us was employed.

The results obtained are given in Table III (p. 792).

The relation between the composition of various mixtures of sodium and potassium nitrates, and the corresponding melting or solidifying points, is shown in Diagram I, the thick broken curve being for the melting points, and the thin broken curve for the solidifying points. By reference to these curves the composition of any mixture of the nitrates may be determined approximately if the melting or solidifying point of the mixture be known. The form of the curves, however, shows that in nearly all cases there are two different mixtures which have the same melting and solidifying points, while mixtures containing from 40 to 50 per cent. of $NaNO_3$ all have the same melting and solidifying points, these points not being affected by alterations in composition between those limits.

II. *Relation of the Solubility to the Fusibility of Isomeric Organic Compounds.*

Raoult Pictet has shown (*Compt. rend.*, **88**, 855), *first*, that the lower the melting point of a solid the longer are the oscillations of its molecules; and *second*, that the melting points of solids correspond to equal lengths of oscillation, so that $t \times w = c$, where t is the melting point measured from the absolute zero, w the length of oscillation, and c a constant.

Of two isomeric bodies, therefore, the one with the lower melting point will, at any given temperature below the melting point, have its molecules moving with oscillations of greater amplitude than the one with the higher melting point. The molecular weights being equal, the force of restitution will be less in the case of the more fusible compound, and hence its molecules will be in a less stable condition, and be the more readily separated from their fellows than those of the less fusible compound. Now in order that a solid may dissolve in any liquid it is necessary that its molecules should undergo a sort of unloosening process, and we should therefore conclude that of two isomeric compounds, that would dissolve the more easily in which the attraction or the force of restitution to the mean position of oscillation was the least, *i.e.*, the one which is the more easily fusible. This argument shows:—

Rule (1.) *That for any series of isomeric organic compounds the order*

TABLE III

Per cent. $NaNO_3$ in original mixture *before* solution.	Mixed nitrates *before* solution.				Mixed nitrates *after* solution and evaporation to dryness.				Per cent. of $NaNO_3$ in the mixture *after* solution and evaporation to dryness, as found :—			
	Uncorrected.		Corrected.		Uncorrected.		Corrected.					
	Melting point.	Solidifying point.	Melting point.	Solidifying point.	Melting point.	Solidifying point.	Melting point.	Solidifying point.	From the melting point.	From the solidifying point.	From analysis.	Average.§
100	303*	—	316†	—	303	—	316	—	100	100	100	100
90	288	286	298	296	284	282	294	292	87·5	88	88·5	88
80	274	266	283	275	259	255	267	263	70	70	75·5	71·8
70	260	255	268	263	—	—	—	—	—	—	—	—
60	238	230	242	237	250	245	256	251	65·5	66	64·7	65·4
50	225	220	231	226	241	236	247	242	61	62·5	63·2	62·2
45·7	225	220	231	226	235	230	242	237	58	60	63·9	60·6
40	225	219	231	226	231	226	238	233	55	56·5	57·0	56·2
30	235	230	242	237	—	—	—	—	—	—	—	—
20	275	275	284	284	225	221	231	227	40	38·5	36·9	38·5
10	295	290	306	300	269	266	278	275	22	22	24·6	22·9
0	—	—	339‡	—	—	—	339	—	0	0	0	0

* By thermometer. † By specific heat method, or 319° by thermometer. ‡ By specific heat method.

§ In taking these averages, no greater weight has been given to the results from analysis than to those deduced from the melting and solidifying points, because the method of analysis employed does not admit of very great exactness, since a very slight error in the weight of mixed sulphates obtained makes a rather large error in the final result.

Note.—M. p. of pure $NaNO_3$ = 314° (Braun, *Pogg. Ann.*, **154**, 190); = 310° (Person, *Ann. Chim. Phys.*, 1847, **22**, 329); = 316° (Carnelley, *Jour. Chem. Soc.*, **33**, 276). S. p. of pure $NaNO_3$ = 298° (Maumené, *Compt. rend.*, **97**, 45). M. p. of pure KNO_3, 342° (Braun, *loc. cit.*); 339° (Carnelley, *loc. cit.*); 339° (Person, *loc. cit.*). S. p. of pure KNO_3 = 327° (Maumené, *loc. cit.*); 320°, Guthrie (*Phil. Mag.* [5], **18**, 114). Schaffgotsch (*Pogg. Ann.*, **102**, 293) gives the following as the solidifying points (corrected) of mixtures of sodium and potassium nitrates :—100 per cent. $NaNO_3$ = 313°; 90 per cent. = 298°; 80 per cent. = 281°; 70 per cent. = 262°; 60 per cent. = 244°; 50 per cent. = 229°; 45·7 per cent. (molec. proportion) = 225·6°; 40 per cent. = 230°; 30 per cent. = 250°; 20 per cent. = 280°; 10 per cent. = 311°; pure KNO_3 = 338·3°.

= 280°; 10 per cent. = 311°; pure KNO_3 = 338·3°.

Formula.	Substance.	Constitution.	M. p.	Order solubili
$C_{20}H_{14}$	Dinaphthyl	α; β	76°	1
	Dinaphthyl	α; α	154	2
	Phenylanthracene	—	152	2
	Dinaphthyl	β; β	187	4
$C_{14}H_{12}Cl_2$	β-Stilbene dichloride	$Ph·C_2H_2Cl_2·Ph$	94	1
	α- „ „	„	192	2
$C_{10}H_6Br_2$	Dibromonaphthalene	—	61	1
	„	—	82	2
	„	—	131	3
$C_4H_6O_4$	Dimethyloxalate	$(CO_2CH_3)_2$	51	1
	Isosuccinic acid	$CO_2H·CH(CH_3)·CO_2H$	130	2
	Succinic acid	$CO_2H·(CH_2)_2·CO_2H$	180	3
$C_6H_{14}O_6$	Sorbitol	—	110	1
	Isodulcitol	—	110*d*	2
	Mannitol	—	162	3
	Dulcitol	—	182	4
$C_8H_6O_4$	Aldehydohydroxybenzoic acid	$CO_2H : OH : COH = 1:2:3$	166	1
	„ „	„ $= 1:3:4$	234	2
	„ „	„ $= 1:4:5$	244	3
	„ „	„ $= 1:2:5$	249	4
$C_8H_8O_4$	Methoxyhydroxybenzoic acid	$CO_2H : OH : OMe = 1:4:5$	207	1
	„ „	„ $= 1:3:4$	250	2
$C_9H_8O_2$	Atropic acid	$Ph·C(CO_2H):CH_2$	106	1
	Cinnamic acid	$Ph·CH:CH·CO_2H$	133	2
$C_9H_8O_5$	Methoxyphthalic acid	$(CO_2H)_2 : OMe = 1:2:4$	141	1
	Methoxyisophthalic acid	„ $= 1:3:2$	217	2
	„ „	„ $= 1:3:4$	261	3
	Methoxyterephthalic acid	„ $= 1:4:5$	278	4
$C_9H_{10}O_3$	Hydrocoumaric acid	$OH : (CH_2·CH_2·CO_2H) = 1:2$	82	1
	Tropic acid	$HO·CH_2·CHPh·CO_2H$	118	2
	Hydroxyxylic acid	$Me_2 : OH : CO_2H = 1:2:4:5$	199	3
$C_9H_{10}O_3$	Methoxytoluic acid	$OMe : Me : CO_2H = 1:4:6$	67	1
	„	„ $= 1:2:6$	81	1
	„	„ $= 1:3:6$	103	1
	„	„ $= 1:2:5$	156	2
	„	„ $= 1:3:4$	176	3
	„	„ $= 1:2:4$	192	4
$C_{10}H_4Br_2O$	α-Dibromocamphor	—	59	1
	β- „	—	114	2
$C_{11}H_{12}Br_2O_3$	Methyl-β-methoxyphenyldibromopropionate	$MeO·C_6H_4·C_2H_2Br_2·CO_2Me = 1:2$	68	1
	Methyl-α-methoxyphenyldibromopropionate	„ „ $= 1:2$	125	2
$C_6H_4O_4N_2$	Dinitrobenzene	$(NO_2)_2 = 1:3$	90	1
	„	„ $= 1:2$	118	2
	„	„ $= 1:4$	172	3
$C_6H_5O_5N_3$	Amidodinitrophenol	$OH : NH_2 : (NO_2)_2 = 1:2:4:6$	165	1
	„	„ $= 1:4:2:6$	170	2
	„	$NH_2 : (NO_2)_2$ = consec.	202	3
$C_6H_{13}O_2N$	Amidocaproic acid	—	170	1
	„	—	subl. 210	2
$C_6H_{14}O_2N$	Amylcarbamide	$NH_2·CO·NH·CH_2·Bu$	120	1
	„	$NH_2·CO·NH·CHMePr$	151	2
$C_7H_5O_4N$	Nitrobenzoic acid	$CO_2H : NO_2 = 1:3$	140	1
	„	„ $= 1:2$	147	2
	„	„ $= 1:4$	238	3
$C_7H_6O_5N_2$	Dinitranisoïl	$OMe : (NO_2)_2 = 1:2:4$	86	1
	„	„ $= 1:2:6$	116	2
$C_9H_{11}O_2N$	Ethamidobenzoic acid	$NHEt : CO_2H = 1:3$	112	1
	Phenyl-β-amidopropionic acid	$Ph·CH(NH_2)·CH_2·CO_2H$	121	1
	Phenyl-α-amidopropionic acid	$Ph·CH_2·CH(NH_2)·CO_2H$	250	2
	α-Amidohydratropic acid	$CH_3·CPh(NH_2)·CO_2H$	w. m. 260°	3
	Phenylmethamidoacetic acid	$NHMe·CHPh·CO_2H$	274°	3
$C_{14}H_{10}O_8N_2$	α-Dinitrodesoxybenzoïn	—	115	1
	β- „	—	126	2
$C_{19}H_{22}ON_2$	Cinchonidine	—	206	1
	Cinchonine	—	245	2
$C_{10}H_6Cl_2O_4S_2$	α-Naphthalenedisulphonyl chloride	$C_{10}H_6(SO_2Cl)_2$	158	1
	β- „ „ „	„	226	2
$C_7H_9ClO_3N_2$	Chlorotoluidine nitrate	$Me : Cl : NH_2 = 1:4:?$	165	1
	„ „	„ $= 1:4:?$	179	2
	„ „	„ $= 1:3:4$	189	3

E IV.

Order of solubility.	One part dissolved by parts solvent.	Solvents.	Authority.
1	—	usual solvents	Smith, *Chem. Soc. Jour.*, **32**, 562.
2	—	„	„ „ „
2	—	„	Schellinger, *Annalen*, **202**, 61.
4	—	„	Smith, *Chem. Soc. Jour.*, **32**, 562.
1	all proportions in alcohol	alcohol	Zincke, *Ber.*, **10**, 999.
2	10 of alcohol	„	„ „
1	—	alcohol	Magatti, *Gazzetta*, **11**, 357.
2	16·5 alcohol at 56°	„	Guareschi, *Annalen*, **222**, 262.
3	50·0 „	„	„ „ „
1	—	water, alcohol, ether	*Watts' Dict.*, **4**, 272.
2	5·5 cold water	water	Wichelhaus, *Zeit. f. Ch.* (2), **3**, 247.
3	20·0 „	water, alcohol, ether	„ „ „
1	0·5 water	water; alcohol	*Watts' Dict.*, **5**, 353; **7**, 1093.
2	2·1 „	„	„ **5**, 1091.
3	6·5 „	„	„ **3**, 823.
4	31·0 „	„	„ **2**, 349.
1	1500 water at 25°	water, alcohol, ether, chloroform	Tiemann, *Ber.*, **10**, 1562.
2	—	„	„ *Ber.*, **12**, 1334.
3	—	„	„ *Ber.*, **9**, 1268.
4	2600 water at 25°	„	„ *Ber.*, **10**, 1562.
1	39 water at 100°	water	Matsmoto, *Ber.*, **11**, 122.
2	155 „ „	„	„ „
1	692 water at 19°	water	*Watts' Dict.*, **6**, 249.
2	3500 „ 17	„	„ „
1	—	water, ether	Schall, *Ber.*, **12**, 829.
2	—	„	„ „
3	—	„	„ „
4	—	„	*Ibid.*; Paternò, *Gazzetta*, **9**, 455.
1	20 water at 18°	water	*Watts' Dict.*, **6**, 715.
2	49 „ 14·5°	„	„ **6**, 249.
3	—	„	Jacobsen, *Ber.*, **12**, 434.
1	—	water	Schall, *Ber.*, **12**, 825.
1	—	„	„ „
1	—	„	„ „
2	—	„	Gerichten, *Ber.*, **11**, 1587.
3	—	„	Schall, *Ber.*, **12**, 825.
4	—	„	„ „
1	4·5 alcohol at 20°	alcohol	Swarts, *Ber.*, **15**, 1662.
2	26·7 „ „	„	„ „
1	28·9 vols. CS_2	carbon disulphide; alcohol	Perkin, *Chem. Soc. Jour.*, **39**, 426.
2	29·6 „	„	„ „ „
1	16·9 alcohol at 24·6°	alcohol, chloroform, ether, benzene, water	Körner, *Gazzetta*, **4**, 305.
2	26·3 „ 24·8	„	„ „ „
3	—	„	Rinne, *Ber.*, **7**, 869.
1	714 water at 22°	water; alcohol	Dabney, *Amer. Chem. J.*, **5**, 20.
2	1219 „ „	„	„ „ „
3	—	„	„ „ „
1	27 cold water	water	*Watts' Dict.*, **3**, 581.
2	43·6 water at 14·5°	„	Nencki, *J. pr. Chem.* [2], **15**, 390.
1	28 water at 27°	water	*Watts' Dict.*, **6**, 1116.
2	79·3 „ „	„	„ „
1	400 water at 10°	water	*Watts' Dict.*, **1**, 555.
2	400 „ 22	—	„ **7**, 947.
3	1327 „ 16	—	„ **6**, 314.
1	64 of 90 p. c. alcohol at 21°	alcohol	Salkowski, *Ber.*, **7**, 370.
2	110 „ „	„	„ „
1	—	alcohol	Griess, *Ber.*, **5**, 1038.
1	—	„	Posen, *Annalen*, **195**, 143.
2	—	„	Schulze, *Ber.*, **14**, 1785.
3	—	„	Tiemann, *Ber.*, **14**, 1976.
3	—	„	„ *Ber.*, **14**, 1982.
1	12 alcohol at 78°	alcohol	Golubeff, *Bull. Soc. Chim.* [2], **34**, 345.
2	24 „	„	„ „ „ „
1	76·4 ether at 10°	ether	Hesse, *Watts' Dict.*, **6**, 463.
2	2118·0 „ at 17	„	„ „
1	7·5 benzene at 14°	benzene, and other solvents	Ebert, *Ber.*, **9**, 598.
2	221·0 „ „	„	„ „
1	19·9 water at 17°	water	Wroblewsky, *Annalen*, **168**, 147.
2	35·5 „ „	„	„ „ „
3	38·5 water at 19°	„	„ „ „

of solubility is the same as the order of fusibility, i.e., the most fusible compound is likewise the most soluble.

In order to test this rule we have collected from literature all the statements which have been made as regards the solubility of isomeric compounds (a task which has involved a very large amount of labour and time), and we have found as follows :—Out of 752 cases in which the rule can be applied, there are 736 in which the order of fusibility and of solubility is the same, and only 16 exceptions (= 2 per cent.) in which the more fusible compound is the less soluble. This is with reference to one solvent in each case, whereas by taking all the solvents into account which have been tried, we have found that out of 1778 cases in which the rule can be applied, there were 1755 which agreed with the rule, and only 23 exceptions (= 1¼ per cent.).

The following may be taken as examples (see Table IV).

This table shows with what a great variety of compounds the rule holds good. Not only do compounds having a similar constitution obey the rule, but compounds likewise which have nothing in common but their isomerism.

The application of the rule, however, does not stop here, for we find that—

Rule (2). *In any series of isomeric acids, not only is the order of solubility of the acids themselves the same as the order of fusibility, but the same order of solubility extends to all the salts of the several acids, so that the salts of the more soluble and more fusible acids are also more easily soluble than the correspondiny salts of the less fusible and less soluble acids.*

We have been able to apply this rule in 143 cases, of which 138 agree with the rule, so that there are only five exceptions, or about 3½ per cent. The following may be given as examples* (see Table V, p. 794).

The above is probably but part of a very general law, viz., that the properties of the corresponding derivatives of two or more isomeric compounds are related to one another in the same way as those of the primitive isomers themselves.

Discussion of Exceptions.—As we have already seen, there are only 28 exceptions out of 1921 cases in which we can apply the rule as to the order of solubility of a series of isomers being the same as the order of fusibility. A list of these exceptions is given in Table VI. In this table the statements as to the solubilities are as nearly as possible verbatim with those given in the original papers.

Of the above 28 exceptions, 12 (viz., Nos. 1, 2, 3, 4, 5, 6, 7, 12, 13, 14, 20, and 21), or nearly one-half, refer to only five sets of isomerides.

* In some instances the melting points of the acids are not known, in which case we have given those of the corresponding acid chlorides or amides instead.

TABLE V.

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
			of acid			
$C_9H_8O_2$ ...	Ca-atropate	$Ph{\cdot}C(CO_2H){:}CH_2$	106°	1	43 at 18°	*Watts' Dict.*, **6**, 249.
	Ca-cinnamate	$Ph{\cdot}CH{:}CH{\cdot}CO_2H$	133	2	608 „	„ „
$C_{11}H_8O_2$ ..	Ca-α-naphthoate.....	$C_{10}H_7{\cdot}CO_2H$	160	1	93 at 15°	*Watts' Dict.*, **6**, 851.
	Ca-β- „	„	183	2	1800 „	„ „
$C_7H_4Cl_2O_2$	Ba-dichlorbenzoate	$CO_2H:Cl_2 = 1:2:6$.....	126	1	21·3 at 4°	*Watts' Dict.*, **8**, 264.
	„ „	„ $= 1:2:3$.....	156	2	37·9 at 16°	„ „
	„ „	„ $= 1:3:4$.....	201	3	90·9 at 18°	„ „
	Cu- „	„ $= 1:2:6$.....	126	1	..	„ „
	„ „	„ $= 1:2:3$.....	156	2	..	„ „
$C_{11}H_7BrO_2$	Ca-α-bromnaphthoate	$C_{10}H_6Br{\cdot}CO_2H$.....	142	1	65·5 at 20°	Hausemann, *Ber.*, **9**, 1521
	„ β- „	„	256	2	5000 „	„ „
	Ba-α- „	„	142	1	59 at 21°	„ „
	„ β- „	„	256	2	4300 „	„ „
	K-α- „	„	142	1	—	„ „
	„ β- „	„	256	2	—	„ „
$C_7H_5IO_3$ ..	Ba-iodosalicylate	$CO_2H:OH:I = 1:2:5$.....	197	1	120 at 8°	Miller, *Ber.*, **16**, 81.
	„ „	„ $= 1:2:3$.....	198	2	190 „	„ „

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
$C_6H_6O_6S_2$.	K-benzenedisulphonate.....	$(SO_3H)_2$ = 1 : 3.....	of chloride 63°	1	—	*Watts' Dict.*, **8**, 251.
	„ „	„ = 1 : 4.....	131	2	—	„ „
	Ba- „ „	„ = 1 : 3.....	63	1	2·2 at 100°	Körner, *Ber.*, **9**, 583.
	„ „	„ = 1 : 4.....	131	2	13·9 „	„ „
	Pb- „ „	„ = 1 : 3.....	63	1	1·2 at 26°	„ „
	„ „	„ = 1 : 4.....	131	2	4·0 „	„ „
$C_7H_6O_3S$..	K-toluenesulphonate	Me:SO_3H = 1 : 3.....	of amide 108°	1 } ?	—	Claessen, *Ber.*, **12**, 1851.
	„ „	„ = 1 : 2.....	136	2 }	—	„ „
	„ „	„ = 1 : 4.....	154	3	—	„ „
	Ba- „ „	„ = 1 : 3.....	108	1	4·4 at 12°	„ „
	„ „	„ = 1 : 2.....	136	2	4·8 „	„ „
	„ „	„ = 1 : 4.....	154	3	26·0 „	„ „
	Na-Ag-Ca or Pb-salt	„ = 1 : 3.....	108	1	—	„ „
	„ „	„ = 1 : 2.....	136	2	—	„ „
		„ = 1 : 4.....	154	3	—	„ „
$C_{10}H_8O_2S$.	Ba-β-naphthalenesulphinic acid	$C_{10}H_7 \cdot SO_2H$	of acid 105°	1	21·5 at 15°	Gessner, *Ber.*, **9**, 1500.
	„ α- „ „	„	high temp.	2	201·0 at 14°	„ „

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
$C_{10}H_8O_3S$.	K-naphthalenesulphonate ..		of amide			
		α	150°	1	13 at 13°	*Watts' Dict.*, **6**, 860.
		β	217	2	15 at 10°	„ „
	Ba- „ „ ..	α	150	1	87 at 10°	„ „
		β	217	2	290 „	„ „
	Ca- „ „ ..	α	150	1	16·5 at 10°	„ „
		β	217	2	76·0 „	„ „
	Pb- „ „ ..	α	150	1	27·0 at 10°	„ „
		β	217	2	115 „	„ „
$C_{10}H_8O_6S_2$	K-naphthalenedisulphonate .	α	158	1	1·4 at 14°	*Watts' Dict.*, **8**, 1356.
		β	229	2	19·2 at 18°	„ „
	Na- „ „	α	158	1	2·2 at 18°	„ „
		β	229	2	8·4 at 19°	„ „
	Ca- „ „	α	158	1	6·2 at 18°	„ „
		β	229	2	16·2 at 19°	„ „
	Ba- or Pb-salt	α	158	1	—	„ „
	„ „	β	229	2	—	„ „
$C_{10}H_{14}O_3S$.	Ba-cymenesulphonate		of acid			
		Me : Prα : SO_3H = 1 : 4 : 2.....	51°	1	40 at 12·5°	Spica, *Ber.*, **14**, 653.
	„ „	„ = 1 : 4 : 3.....	87	2	214 „	„ „
$C_9H_{11}O_4SN$	Ba-sulphamine mesitylenate .	$Me_2:(SO_2{\cdot}NH_2):CO_2H$ = 1 : 3 : 4 : 5	263	1	30·6 at 0°	Jacobsen, *Ber.*, **12**, 606.
	„ „	„ = 1 : 3 : 2 : 5	276	2	48·8 „	„ „

	„	„	„	=1:3:2:5	270	2	48·8 „	„	„

No.	Formula.	Name.	Constitution.	M. p.	O of bil
1, 2, & 3.	$C_4H_6O_5$	Glycollic anhydride.....	$HO{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CO_2H$	129°	
		Diglycollic acid	$O(CH_2{\cdot}CO{\cdot}OH)_2$.....	148	
4 & 5.	$C_5H_8O_4$	Dimethyl malonate.....	$CH_2(CO_2Me)_2$.....	liquid	
		Ethylmalonic acid	$CHEt(CO_2H)_2$.....	112°	
		Dimethylmalonic acid	$CMe_2(CO_2H)_2$.....	170	
6 & 7.	$C_{11}H_{12}O_3$	β-Ethoxyphenylacrylic acid	$OEt:(C_2H_2{\cdot}CO_2H) = 1:2$	135	
		β-Methoxyphenylcrotonic acid...	$OMe:(C_3H_4{\cdot}CO_2H) = 1:4$	154	
		Butyrocoumaric acid.....	$(C_4H_7O):CO_2H = 1:2$	174 p.d.	
8.	$C_{21}H_{14}O$.....	ββ-Dinaphthylketone	$CO(C_{10}H_7)_2$	125	
		αα- „ „	„	135	
		ββ- „ „	„	165	
9.	$C_{12}H_6N_2$.....	γ-Dicyanonaphthalene.....	$C_{10}H_6(CN)_2$	204	
		c- „ „	„	236	
10.	C_6H_5IO	Iodophenol	$OH:I = 1:3$ (?)	65	
		„	„ $= 1:4$ (?)	89	
11.	$C_7H_5IO_3$.....	Iodosalicylic acid	$CO_2H:OH:I = 1:2:5$	197	
		„ „	„ $= 1:2:3$	198	
12, 13, & 14.	$C_5H_{11}O_2N$	γ-Hydroxyvaleramide.....	$CH_3{\cdot}CH(OH){\cdot}(CH_2)_2{\cdot}CO{\cdot}NH_2$	50	
		Ethyllactamide	$CH_3{\cdot}CH(OEt){\cdot}CO{\cdot}NH_2$	63	
		α-Methoxybutyramide.....	$CH_3{\cdot}CH_2{\cdot}CH(OMe){\cdot}CO{\cdot}NH_2$	78	
		α-Hydroxyisovaleramide	$CHMe_2{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$	104	
15.	$C_7H_4O_6N_2$	Dinitrobenzoic acid	$CO_2H:(NO_2)_2 = 1:3:4$	161 u.c.	
			„ $= 1:2:4$	181	
16.	$C_8H_7O_4N$.....	Aldoxime salicylic acid	$CO_2H:OH:(CH{:}NOH) = 1:2:5$..	179	
			„ $= 1:2:3$..	193	
17.	$C_9H_7O_6N$.....	α-Nitrouvitic acid.....	$(CO_2H)_2:Me:NO_2 = 1:3:5:2$	227	
		β- „ „	„ $= 1:3:5:4$	250	
18.	$C_{10}H_6O_5N_2$.....	Dinitro-α-naphthol.....	$OH:(NO_2)_2 = \alpha_1\alpha_2\beta_1$;	138	
		„ -β- „	„ $= \beta_1$?; β_1.....	197	
19.	$C_{11}H_{14}O_2N_2$.....	Tolusuccinamide	$Me:(NH{\cdot}CO{\cdot}C_2H_4{\cdot}CO{\cdot}NH_2) = 1:4$.	148	
		„ „	„ $= 1:2$.	160	
20 & 21.	$C_{16}H_{15}O_3N$.....	α-Ethyldibenzhydroxamate.....	NBz_2EtO.....	58	
		β- „ „	„	63	
22.	$C_3HClBr_2O_2$	β-Chlordibromacrylic acid.....	$CBr_2{:}CCl{\cdot}CO_2H$	99	
		α- „ „	$CBrCl{:}CBr{\cdot}CO_2H$	104	
23.	$C_9H_{11}O_4SN$	Sulphaminemesitylenic acid	$Me_2:CO_2H:(SO_2{\cdot}NH_2) = 1:3:5:6$.	263	
		„ „ „	„ $= 1:3:5:2$.	276 d.	
24.	From $C_{12}H_{12}O_4$....	Ammonium α-hydropiperate.....	—	of acid 78°	
		„ β- „	—	131	
25.	From $C_{15}H_{10}O_2$....	Na-β-phenanthrenecarboxylate ..	$C_6H_4{\cdot}CH{:}C(CO_2H){\cdot}C_6H_4$	251	
		„ -α- „ „ ..	$C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_3{\cdot}CO_2H$	266	
26.	From $C_5H_2Br_2O_2$..	Ca-dibrompyromucate.....	$O{\cdot}CBr{:}CH{\cdot}CBr{:}C{\cdot}CO_2H$.....	168	
		„ „	$O{\cdot}CH{:}CBr{\cdot}CBr{:}C{\cdot}CO_2H$.....	192	
27.	From $C_6H_7O_2N$ ...	Pb-β-methylcarbopyrollate.....	$C_4H_3MeN{\cdot}CO_2H$	142	
		„ -γ- „ „	„	169	
28.	From $C_3HClBr_2O_2$	Ca-β-chlordibromacrylate	$CBr_2{:}CCl{\cdot}CO_2H$	99	
		„ -α- „ „	$CBrCl{:}CBr{\cdot}CO_2H$	104	

Table VI.

p.	Order of solubility.	1 part dissolved by parts solvent.	Authority.	Remarks.
	2	insoluble in alcohol, ether, and water	*Watts' Dict.*, **7**, 570	Three exceptions, since they are exceptions as regards all three solvents. The symmetry accords with the m. p. but not with the solubility. Diglycollic acid crystallises with 1 mol. H_2O. Would this affect the solubility?
	1	easily soluble in alcohol, water, and sparingly in ether	„ **2**, 913	
d	3	insoluble in water	Osterland, *Ber.*, **7**, 1286	—
	1	easily soluble.....	Markownikoff, *Annalen*, **182**, 62	—
	2	sparingly soluble	„ „ „	—
	2	not very soluble in alcohol	Perkin, *Ch. Soc. Jour.*, **39**, 414	Does the butyrocoumaric acid form a compound with alcohol?
	2	moderately soluble.....	„ „ **31**, 412	
o.d.	1	extremely soluble.....	„ „ **21**, 476	
	2	267 alcohol at 19°	*Watts' Dict.*, **8**, 1157	The modification melting at 125° is said to be a physical isomeride of that melting at 165°.
	1	77 „ 14	„ „	
	3	1256 „ 19	„ „	
	2	slightly soluble in alcohol.....	*Watts' Dict.*, **6**, 848	cf. *Zeitsch. f. Chem.* [2], **5**, 571.
	1	easily „ „	„ „	
	2	sparingly soluble in water.....	Lobanoff, *Ber.*, **6**, 1251.....	The symmetry accords with the m. p. but not with the solubility.
	1	readily „ „	„ „	
	2	more difficultly soluble in water	Miller, *Ch. Soc. Jour.*, **41**, 404.	M. ps. very close. The Ba-salts obey the rule.
	1	„ easily „ „	„ „ .	
	3	insoluble in ether.....	Neugebauer, *Annalen*, **227**, 97	—
	1	soluble in ether	*Watts' Dict.*, **3**, 452	—
	1	„ „	Duvillier, *Compt. rend.*, **88**, 598	—
	2	sparingly soluble in ether.....	Lipp, *Annalen*, **205**, 1.....	—
a.c.	2	148 water at 25°.....	Claus, *Ber.*, **13**, 816.....	—
	1	54 „ „	„ „	—
	2	pretty easily soluble in hot water	Fürth, *Ber.*, **16**, 2182	The 1 . 2 . 5-compound crystallises with 1 mol. H_2O, whereas the other is anhydrous. Was the m. p. determined with the former in the anhydrous state?
	1	distinctly less soluble in hot water	„ „	
	2	crystallises first from water ...	Böttinger, *Ber.*, **9**, 806	The symmetry accords with the solubility but not with the m. p. The *a*-compound contains $2H_2O$, and the *β*-compound $\frac{1}{2}H_2O$. Were the m. ps. determined in the anhydrous state?
	1	„ second „ ...	„ „	
	2	slightly soluble in ether	*Watts' Dict.*, **6**, 856	The salts obey the rule.
	1	very „ „	Wallach, *Ber.*, **3**, 846	
	2	less soluble } solvent not.....	Bechi, *Ber.*, **12**, 321.....	The symmetry accords with the solubility but not with the m. p. The corresponding imides agree with the rule both as to symmetry and solubility. Have not the m. ps. got transposed in the original paper?
	1	more „ } stated	„ „	
	2	easily soluble in alcohol and ether	Gürke, *Annalen*, **205**, 279	(cf. *Annalen*, **175**, 326). M. ps. very close. These are physical isomerides.
	1	more easily soluble in alcohol and ether	„ „ „	
	2	37·1 water at 20°	Mabery, *Am. Ch. J.*, **6**, 157 ...	Ba-salts obey the rule, Ca-salts do not (see No. 28); m. ps. very close. The symmetry accords with the solubility but not with the m. p.
	1	18·4 „ „	„ „ „ ...	
	2		Jacobsen { *Ber.*, **12**, 604	Ba- and Ca-salts obey the rule. The symmetry accords with the m. p. but not with the solubility.
	1	much more easily soluble in [hot water	*Annalen*, **206**, 167	
			„ „ „	
d	2	less soluble } solvent not.....	Buri, *Annalen*, **216**, 172.....	The acids obey the rule.
	1	more „ } stated	„ „ „	
	2	16·1 water at 20°	Japp, *Ch. Soc. Jour.*, **37**, 86...	The acids and Ba-salts obey the rule. Solubilities very close.
	1	14·7 „ „	„ „ ...	
	2	very difficultly soluble in water	Hill, *Ber.*, **17**, 1759.....	The acids obey the rule.
	1	more easily „ „	„ „	
	2	difficultly soluble } solvent not	Ciamician, *Ber.*, **14**, 1057.....	Pb-salts were not analysed; one or other might have been a basic salt. Relative solubility of free acids not stated.
	1	easily soluble } stated	„ „ „	
	2	less soluble in water	Mabery, *Am. Ch. J.*, **6**, 157 ...	The acids are also exceptions. Ba-salts obey the rule. The m. ps. are very close (see No. 22). The symmetry accords with the solubility but not with the m. p.
	1	more „ „	„ „ „ ...	

The above 28 exceptions may be classified thus :—

(1.) Five are only barely exceptions, the melting points being very close, viz., Nos. 11, 20, 21, 22, and 28. The information given in respect to these is not sufficient to allow one to say whether the solubilities are correspondingly close, except in No. 22 (*q.v.*).

(2.) In No. 25 the solubilities of the compounds compared are very nearly equal, whilst the melting points are not very different.

(3.) In No. 27 the two Pb salts referred to were not analysed, and one or other of them might have been a basic salt, and therefore not really isomeric and comparable with the other one.

(4.) Seven, though exceptions themselves, yield salts which obey the rule (viz., Nos. 11, 18, 19, 22, 23, 25, 28).

(5.) Three salts, which are exceptions, are derived from acids which obey the rule (viz., Nos. 24, 25, 26).

(6.) Three (viz., Nos. 8, 20, 21) are physical and not chemical isomerides in the ordinary sense, and our knowledge of the so-called physical isomerides is at present very limited.

(7.) In five (viz., Nos. 1, 2, 3, 10, and 23) the solubilities are exceptional, not only as regards the melting points, but also as regards the symmetry. (The more symmetrical of two isomerides is usually less soluble than the one in which the atomic arrangement is less symmetrical.)

(8.) In five (viz., Nos. 4, 17, 12, 22, 28) the melting points are not only exceptional as regards the solubilities, but also as regards the symmetry. (The more symmetrical of two isomerides usually has the higher melting point.)

(9.) In two (Nos. 16 and 17) one or other of the isomerides contains water of crystallisation, and it is not stated whether the melting point was determined with the anhydrous compound. If made with the hydrated compound, the water would be driven off on heating, and collect in the upper part of the melting point tube, and might run down and lower the melting point of the substance, if proper care were not taken.

(10.) Eight (viz., Nos. 5, 6, 7, 9, 12, 13, 14, 15) are not included in any of the above classes, and so far as one can learn from the statements published in reference to these compounds, there is nothing to lead one to suppose but that they are real exceptions to the rule. We may say, therefore, that out of the 1921 cases in which the rule can be applied, there are only from 9 to 12 exceptions ($= \frac{8}{3}$ per cent.) against which, so far as one can see at present, no objection can be raised. It is possible, however, that most, if not all, of these exceptions may on further investigation turn out to be due to errors either in the determination of the melting points or of the solubilities, or possibly to clerical errors.

The relation between fusibility and solubility may also be illustrated by a great number of cases other than those of isomeric compounds. Among these the following are noteworthy :—

(*a.*) *Allotropic Modifications of the same Element.*—(1.) *Phosphorus.* Common or yellow phosphorus melts at 44°, and is readily soluble in carbon disulphide, chloride of sulphur, phosphorus trichloride, and phosphorus pentasulphide, and slightly soluble in ether, turpentine, and the essential oils; whereas red phosphorus, which does not melt below 255°, is insoluble in all these solvents. (2.) *Sulphur.* Common or octahedral sulphur melts at 114·5° (Brodie), and is readily soluble in carbon disulphide; whereas plastic sulphur does not melt at 120° (? Brodie), and is insoluble in carbon disulphide. (3.) *Selenium.* Amorphous selenium melts at a little above 100° (Berzelius), and is soluble in carbon disulphide and in benzene; whereas crystalline selenium melts at 217° (Hittorf), and is quite insoluble in carbon disulphide or in benzene.

(*b.*) *Paraffin Wax.*—The solubility of paraffin wax in benzene is less the higher its melting point, as may be seen from the following table (*Watts' Dict.*, **7**, 893) :—

M. p.	Quantity of paraffin wax deposited at 18° by 100 c.c. of refined benzene.
35·0°	133 grams.
49·6	6 „
52·8	4·7 „
65·5	1·4 „
80·0	0·1 „

(*c.*) *Mixtures of Sodium and Potassium Nitrates.*—Table VII (p. 799), which embodies the results of the determinations already given in detail, will show the relations which subsist between the fusibility and solubility of mixtures of sodium and potassium nitrates :—

These results are also shown graphically in Diagrams I and II. Diagram I gives the curves of fusibility and two curves of solubility; in one of the latter, the solubility is referred to the percentage composition of the mixed nitrates *before* solution, and in the other to the composition of the mixed nitrates *after* solution and evaporation to dryness. Diagram II gives the curves, showing the actual weights of sodium and potassium nitrates respectively, dissolved from various mixtures of the two salts, and compares these with the curves of total solubility of the mixed salts.

An inspection of the above table and accompanying diagrams shows :—

(*α.*) As regards the fusibility and total solubility of the mixed nitrates (see Diagram I) :—

TABLE VII.

Per cent. of $NaNO_3$ in original mixture *before* solution.	Melting point (cor.) of mixture *before* solution.	Total weight of mixed salts dissolved by 100 parts of water at 20°	=	Weight of $NaNO_3$ dissolved.	+	Weight of KNO_3 dissolved.	Per cent. of $NaNO_3$ in the mixture *after* solution and evaporation to dryness.	Melting point (cor.) of the mixed nitrates *after* solution.
100	316°	86·8		86·8		0	100	316°
90	298	109·6		96·4		13·2	88	294
80	283	136·5		98·0		38·5	71·8	267
70	268	136·3		—		—	—	—
60	242	137·6		90·0		47·6	65·4	256
50	231	106·1		66·0		40·1	62·2	247
45·7*	231	88·0		53·3		34·7	60·6	242
40	231	81·1		45·6		35·5	56·2	238
30	242	73·5		—		—	—	—
20	284	54·1		20·8		33·3	38·5	231
10	306	40·9		9·4		31·5	22·9	278
0	339	33·6		0		33·6	0	339

* = $NaNO_3 + KNO_3$.

(1.) That the *fusibility* gradually increases from pure $NaNO_3$ (m. p. 316°), until the mixture contains about 50 per cent. $NaNO_3$, and melts at 231°; the melting point then remains constant until the sodium nitrate falls to 40 per cent., after which the fusibility gradually diminishes until pure KNO_3 (m. p. 339°) is reached. A mixture having the molecular composition ($NaNO_3 + KNO_3$) contains 45·7 per cent. $NaNO_3$. According to Schaffgotsch (*Pogg. Ann.*, **102**, 293) the salts when mixed in molecular proportion melt at a lower temperature than when present in any other.

(2.) That, starting with pure sodium nitrate, the total solubility quickly increases until the proportion of the $NaNO_3$ in the mixture before solution falls to 80 per cent., after this it remains constant until the $NaNO_3 = 60$ per cent., beyond which the solubility rapidly diminishes until pure potassium nitrate is reached. A mixture containing about 45·7 per cent. $NaNO_3$ ($= NaNO_3 + KNO_3$) dissolves to about the same extent at 20° as pure sodium nitrate, whereas all mixtures containing a smaller proportion of sodium nitrate are less soluble than the pure salt. The above refers to the proportion in which the salts are mixed *before* solution; if, however, the solubilities be referred to the proportion between the two salts in the residue obtained by evaporation of the saturated solution, we find that though the general form of the curve is very similar to that in the first case, yet the solubility is constant over a much smaller range of variation in the composition of the mixed salts. Thus the maximum of solubility is

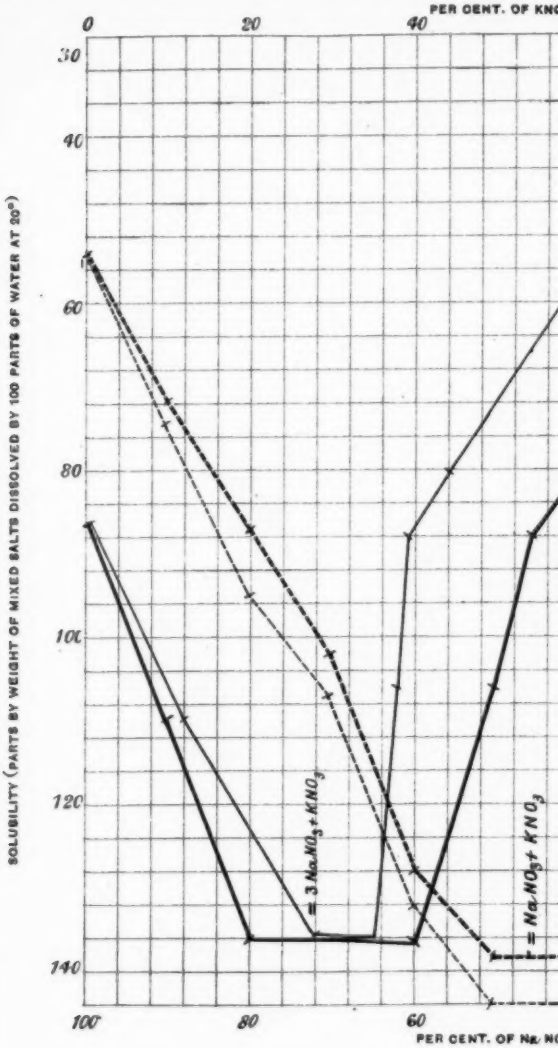
obtained when the sodium nitrate falls to 72 per cent., and continues constant at this until the sodium nitrate falls to 65 per cent., after which it rapidly diminishes to pure potassium nitrate. It will thus be seen that the depression of the curve, based on the composition of the mixture *after* solution and evaporation, lies throughout its whole course within that of the curve, based on the composition of the mixture *before* solution. This shows that before the maximum of solubility is reached the proportion of sodium nitrate in the dissolved portion is less than in the mixture before solution, whilst beyond that point it is greater. In other words, starting with pure sodium nitrate, there is a smaller proportion of sodium nitrate in solution than in the original mixture until the point of maximum solubility is reached, after which the proportion of sodium nitrate in solution is greater than in the original mixture before solution.

(3.) That the general form of the four curves (two of fusibility and the other two of solubility) in Diagram I is very similar, showing an intimate connection between them. The two curves of solubility, however, differ from those of fusibility in one important particular, in that, starting from the pure sodium nitrate end, the maxima of the two solubility curves occur earlier than those of the curves of fusibility. Thus, whereas the middle of the maximum of fusibility occurs when the composition of the mixture corresponds with the formula ($NaNO_3 + KNO_3$), that of the two solubility curves corresponds approximately with the composition ($3NaNO_3 + KNO_3$). That is to say, the addition of potassium nitrate to the pure sodium salt affects the solubility more quickly than it does the fusibility, whereas the addition of sodium nitrate to pure potassium nitrate increases the fusibility more rapidly than it does the solubility.

(β.) As regards the solubilities of the sodium and potassium nitrates respectively in the presence of one another (see Diagram II) :—

(4.) That the solubility of pure potassium nitrate at 20° (Curves B_1 and B_2) is scarcely, if at all, affected by the addition thereto of the sodium salt, unless the amount of the latter present in the mixture reaches about 45 per cent. before solution, or 60 per cent. in the dissolved portion. Thus a solution of pure potassium nitrate, saturated at 20°, contained 33·6 parts by weight of the pure salt in 100 parts of water, while a saturated solution obtained by treating a mixture consisting of 20 per cent. $NaNO_3$, and 80 per cent. KNO_3, contained 33·3 parts of potassium nitrate, and one obtained by treating a mixture consisting of 45·7 per cent. $NaNO_3$, and 54·3 per cent. KNO_3, contained 34·7 parts of potassium nitrate. The residues obtained by evaporating the several saturated solutions to dryness weighed 33·6, 54·1, and 88·0 grams respectively, and contained 0, 38·5, and 60·6 per cent. of sodium nitrate. When the mixture contains more than

I. DIAGRAM OF THE SOLUBILITY AND FUSIBILITY OF MIXT



REFERENCE.

Curve of Total Solubility and % composition of mixture be

——— *Ditto* ——— *ditto* ———

Curve of Melting Points of mixed Nitrates .....

Curve of Solidifying Points of ditto .....

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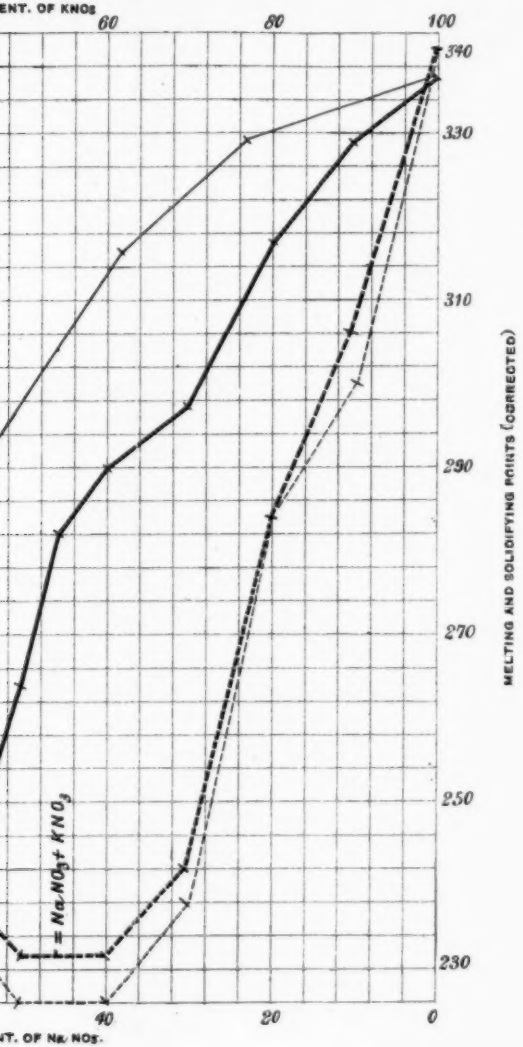
Y OF MIXTURES OF SODIUM AND POTASSIUM NITRATES.



FERENCE.

mixture before *solution* .....

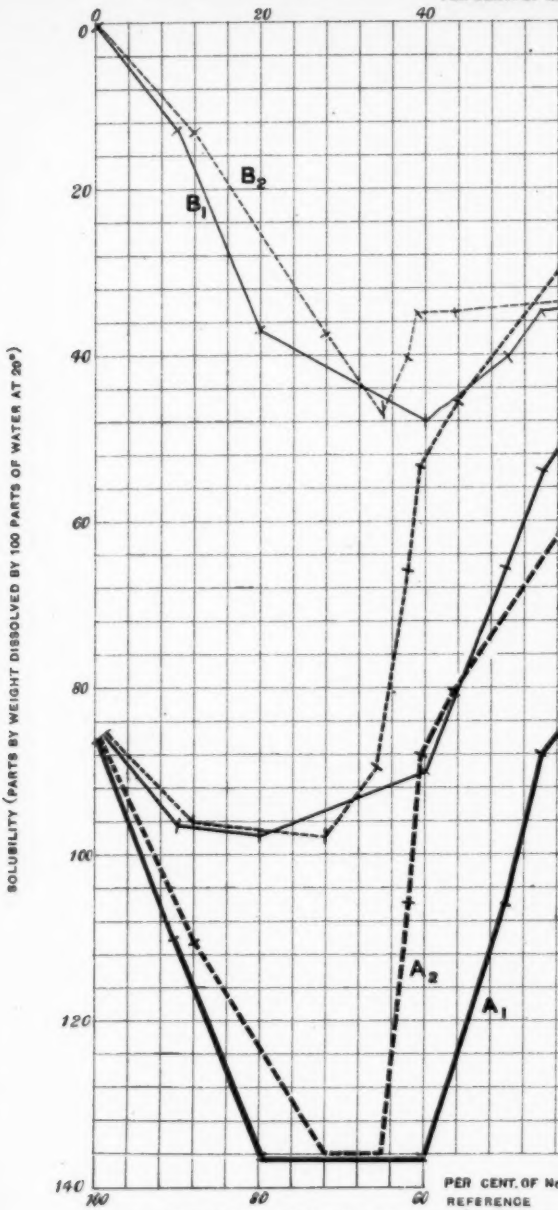
after *solution and evaporation* .....

.....

.....

Lith. St Martins Lane W.C.

II. DIAGRAM OF SOLUBILITY FOR MIXTURES OF



A_1 = *Curve of Total Solubility of Mixture and % compos*

A_2 = ___ *Ditto* _____ *di*

B_1 = *Curve of Solubility of* KNO_3 *and % composition of*

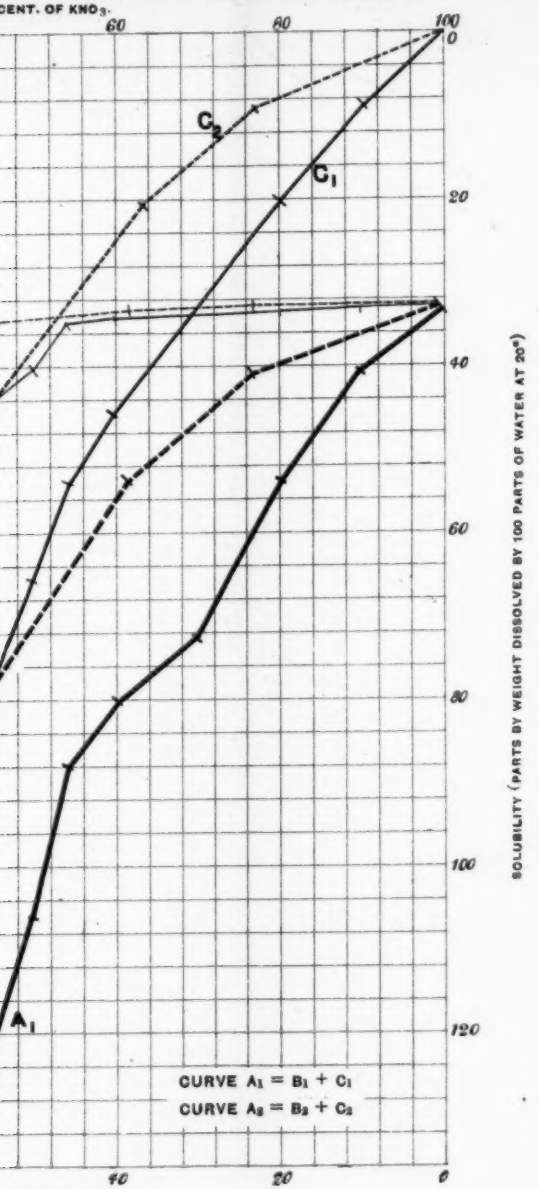
B_2 = ___ *Ditto* _____ *ditto* ___

C_1 = *Curve of Solubility of* $Na\,NO_3$ *and % composition*

C_2 = ___ *Ditto* _____ *ditto* ___

Harrison & Sons. Lith. St Martin

TURES OF SODIUM AND POTASSIUM NITRATES



FERENCE

d % composition of mixture before *solution* ——————

——— *ditto* ——— after *solution* - - - - - -

position of mixture before *solution* ------ ——————

ditto ——— after *solution* ------ ----------

omposition of mixture before *solution* ----- ——————

to ——— after *solution* ---------- - - - - - -

Lith. S. Martins Lane, W.C.

45 per cent. of sodium nitrate, the weight of the potassium salt dissolved increases, until the former salt reaches about 60 per cent., after which it rapidly diminishes, until the salt consists of pure sodium nitrate. The weight of potassium nitrate dissolved by a given weight of water at 20° from a mixture containing 82 per cent. of sodium nitrate, is also the same as that dissolved from pure potassium nitrate by the same weight of water at the same temperature.

(5.) That the solubility of pure sodium nitrate at 20° (Curves C_1 and C_2) is at first somewhat increased by admixture with potassium nitrate; this continues until the latter reaches about 20 per cent., after which the solubility of the sodium salt, at first slowly, and then rapidly, diminishes, until the salt consists of pure potassium nitrate.

III. *Influence of the Nature of the Solvent.*

If it be true that the more fusible compound is also the more soluble, it follows that:—

Rule (3). *For any series of isomeric compounds the order of solubility is the same, no matter what may be the nature of the solvent.*

We have been able to apply this rule in 666 cases, and find that the whole of these, without a single exception, accord with the rule. A few examples in illustration of this rule are given in Table II. It holds good not only with acids but also with their salts, so far, at least, as the solubilities of such salts have been tested in solvents other than water (cf. Rule 2). It further holds in many other cases, *e.g.*, the two allotropic modifications of phosphorus, of sulphur, and of selenium (see above, p. 798).

With the view of submitting this rule to a very stringent test we have determined the solubility of meta- and para-nitraniline in 13 different solvents, with the results given in Table VIII, p. 802.*

This table shows, therefore, that no matter what the nature of the solvent, the meta-nitraniline is always more soluble than the para-compound.

The table further shows that:—

Rule (4). *The ratio of the solubilities of the two isomerides in any given solvent is very nearly constant, and is therefore independent of the nature of the solvent.*

This ratio varies from the extreme limits of 1·15 in the case of methyl alcohol, in which the nitranilines are most soluble, to 1·48 in water, in which they are least soluble. The ratios for the other solvents, however, lie very much nearer to the mean value 1·29, the greatest deviation from it, in their case, being confined to the second decimal place.

* For details of these determinations see Table I.

TABLE VIII.

Solvent.	Weight of substance dissolved by 100 parts by weight of solvent.		Ratio. $\frac{\text{meta-}}{\text{para-}}$.
	Meta-.	Para-.	
Water, H_2O	0·114	0·077	1·48 highest
Methyl alcohol, CH_4O	11·06	9·59	1·15 lowest
Ethyl alcohol, C_2H_6O	7·05	5·84	1·21
Propyl alcohol, C_3H_8O	5·65	4·35	1·30
Isobutyl alcohol, $C_4H_{10}O$	2·64	1·91	1·38
Isoamyl alcohol, $C_5H_{12}O$	8·51	6·29	1·35
Ethyl ether, $C_4H_{10}O$	7·89	6·10	1·29
Benzene, C_6H_6	2·45	1·98	1·24
Toluene, C_7H_8	1·71	1·31	1·31
Cumene, C_9H_{12}	1·15	0·90	1·28
Chloroform, $CHCl_3$	3·01	2·31	1·30
Carbon tetrachloride, CCl_4	0·21	0·17	1·24
Carbon disulphide, CS_2	0·33	0·26	1·27
	—	Mean =	1·29

It will be noted that the solvents employed are numerous and very varied in character, whilst at the same time the range in solubility is very great, varying in the case of the para-compound from 0·077 in water to 9·59 in methyl alcohol, in the latter of which, therefore, it is 124 times more soluble than in water. This forms a very crucial test, at least so far as regards the order of solubility.

Up to the present we have only completed experiments with this single pair of compounds, but we are extending the work to other series of isomerides. If this further work confirms the above results, then the solubility of any pair of isomerides A and B will be represented by the following expression, which is independent of the nature of the solvent :—

$$\frac{\text{Solubility of A in any solvent}}{\text{Solubility of B in the same solvent}} = \text{constant}$$

(for any given temperature). So that if the solubility of A in any solvent at a given temperature be known, that of B at the same temperature may be calculated. The influence of temperature on the above ratio is at present under investigation, and we are also engaged with the determination of the solubility of isomerides at temperatures equidistant from their melting points.

The bearing of the above results on the general question of the nature of solution will be discussed later in connection with other data obtained on entirely independent lines, but all leading to the same point.

LXV.—*The Action of Chromium Oxychloride on Orthosubstituted Toluenes.*

By Charles M. Stuart, M.A., Fellow of St. John's College, Cambridge, and W. J. Elliott, Scholar of Christ's College, Cambridge.

It is well known that the action of chromium oxychloride on the homologues of benzene gives rise to the formation of solid compounds which consist of 1 molecule of the hydrocarbon combined with 2 molecules of the oxychloride, and which are decomposed by water with the formation of aldehydes.

V. v. Richter (*Berichte*, **19**, 224) has examined the action of chromium oxychloride on orthonitrotoluene; but although he succeeded in showing the production of a small quantity of orthonitrobenzaldehyde, he found that for the most part orthonitrotoluene was re-formed.

We have examined the interaction of ortho-haloïd derivatives of toluene and chromium oxychloride.

Ten grams of the substituted toluene dissolved in carbon bisulphide were added very gradually to a solution of 25 grams of chromium oxychloride in the same liquid, which was kept cool by a stream of water. The mixture was allowed to stand three days; the solid was then filtered off and added to water. A heavy oil separated, and the solution contained, in all cases, a salt of chromium and chromic acid. The chromic acid was reduced by a current of sulphur dioxide.

Orthochlorotoluene and Chromium Oxychloride.

The chief part of the oil which separated distilled at 205° to 210°. The substance formed a crystalline compound with sodium hydrogen sulphite solution, and gave, with malonic acid, an acid melting at 192° with effervescence, namely, orthochlorobenzalmalonic acid.

0·5011 gram take 36 c.c. N/10 $AgNO_3$ solution = 25·50 p. c. Cl.
Theory for $C_6H_4Cl{\cdot}COH$ = 25·25 „

It is, therefore, orthochlorobenzaldehyde.

In this experiment we were unable to isolate any other compound.

Orthobromotoluene and Chromium Oxychloride.

When the oil which separated was distilled, it came over in two fractions; the first at 215—220°, the second at 225—235°.

The first fraction (215—220°) gave, with sodium hydrogen sulphite solution, a crystalline precipitate, and with malonic acid an acid melting at 198° with effervescence, namely, orthobromobenzalmalonic acid.

0·1843 gram required 10 c.c. N/10 $AgNO_3$ solution = 43·40 p. c. Br.
Theory for $C_6H_4Br{\cdot}COH$ = 43·24 „

It is, therefore, orthobromobenzaldehyde.

The second fraction (225—235°) was shaken with sodium hydrogen sulphite solution, and then with ether. The residue obtained by distilling off the ether from the ethereal solution was found to contain both chlorine and bromine.

0·1604 gram required 20 c.c. N/10 $AgNO_3$ solution before boiling with PbO_2, and 13·4 c.c. after boiling with PbO_2.

0·2496 gram gave 0·3149 gram CO_2 and 0·0662 gram H_2O.

	Found.		Theory for $C_6H_4Br{\cdot}CHCl_2$.
C.....	34·41	C.....	35·00
H	2·92	H.....	2·07
Cl.....	29·65	Br	33·33
Br	32·91	Cl	29·58

When boiled with potash solution it is converted into the aldehyde. Its formula is, therefore, $C_6H_4Br{\cdot}CHCl_2$. It is partially decomposed on distillation with evolution of hydrogen chloride.

Orthiodotoluene and Chromium Oxychloride.

When the oil was distilled, the temperature rose slowly to 270°. The distillate was shaken with sodium hydrogen sulphite solution. The larger portion remained as an oil.

The aqueous solution was shaken with ether in order to extract all oil that remained. Hydrogen chloride was then added and the solution boiled; a slight smell of aldehyde could be detected, and there were drops of oil on the condensing tube.

A trace of aldehyde only is produced.

The oil which remained after shaking with sodium hydrogen sulphite solution, was shaken with sodium thiosulphate solution in order to remove all free iodine. The residue boiled with decomposition at 243—250°.

0·3764 gram required 38 c.c. N/10 $AgNO_3$ solution.
12·7 c.c. N/10 $Na_2S_2O_3$ solution.

0·4475 gram gave 0·1013 gram H_2O and 0·4747 gram CO_2.

	Found.		Theory for $C_6H_4I{\cdot}CHCl_2$.
C.....	28·92	C.....	29·26
H.....	2·51	H.....	1·74
I.....	45·01	I.....	44·25
Cl.....	24·35	Cl.....	24·42

The substance is, therefore, orthiodobenzal chloride. When boiled with potash it is converted into aldehyde.

These experiments, therefore, prove that the action of water on the solid compounds of chromium oxychloride and ortho-substituted toluenes is to produce, in the first instance, an ortho-substituted benzal chloride, of the formula $C_6H_4X{\cdot}CCl_2H$; but that this in the case of the orthochlorotoluene is entirely, and in the case of the orthobromotoluene partially, decomposed by water with the formation of an aldehyde; while the orthiodo-compound is scarcely affected. It is extremely probable that the formation of all aromatic aldehydes by this method is preceded by the formation of derivatives of benzal chloride.

For this reason we examined the reaction between orthonitrotoluene and chromium oxychloride. Like V. v. Richter, however, we found that a trace of orthonitrobenzaldehyde only was produced, while not a trace of a compound containing chlorine was formed, but the greater part of the orthonitrotoluene was reproduced.

LXVI.—*The Molecular Weight of Iodine in its Solutions.*

By Morris Loeb, Ph.D.

It is a matter of everyday observation that iodine has the property of dissolving with different colours in different liquids; in some it shows the reddish-brown hues of its solid and liquid states; in others it acquires the violet colour so characteristic of its vapour. The inference seems very natural that this diversity of colour must depend on a different form of aggregation of the iodine-atoms within the solvent. Since the molecules of solids and liquids appear to be more complex than those of gases, we might suppose that the red solutions contain more complex molecules of iodine than do the violet ones. This is, in fact, the usual assumption; but apart from certain qualitative indications, there has been no proof of its truth; quantitative evidence has not yet been forthcoming in support of the hypothesis. That I have been fortunate in obtaining such, I owe to those new

means of investigating the state of dissolved matter with which the happy generalisations of Raoult, and the skilful mathematical deductions of van't Hoff, have furnished us. I refer to the phenomena of "osmotic pressure," which can be measured by the depression of freezing point and vapour-tension which liquids experience when mingled with a foreign substance. By the advice of Professor Ostwald, I undertook to attack the problem of the molecular weight of iodine in its solutions by the vapour-tension method, and I now give the results of the experiments carried out under his direction at the Chemico-Physical Laboratory of Leipsic University.

Two liquids at once presented themselves as the appropriate solvents, ether and carbon bisulphide; they both have a considerable vapour-tension, and they may be considered as typical of the two kinds of solvents for iodine. For, whereas many iodine solutions show impure tints, that in ether is of a deep reddish-brown, and that in carbon bisulphide of a pure violet. It was not so easy to find a proper apparatus, as Raoult's was quite inapplicable. He operates in the Torricellian vacuum, and has merely to note the comparative heights of the mercury when the solution and the pure solvent are introduced above it. In the case of iodine, all contact with mercury must obviously be avoided. After various attempts, the following apparatus was devised, which is an adaptation of Regnault's manometer to the

present purpose. It consists of two bottles of nearly equal capacity, provided with carefully ground, hollow glass stoppers. To these stoppers, glass tubes are adapted, 60 cm. long, and of about 6 mm. bore, which are bent twice at right angles, so that there is an ascending limb and a horizontal piece of 10 cm. length each, and a descending limb, 40 cm. long, for each half of the apparatus. The lower ends of these two tubes are connected with each other by means of a T-tube, to which they are joined by short pieces of very stout rubber tubing; the third end of the T-tube serves as a communication with the exterior when needed, and carries a rubber tube with pinch-cock. The communication between the two halves of the apparatus can also be interrupted by means of a pinch-cock on one of the rubber joints. Into one of the bottles, the iodine solution is placed, whilst the pure solvent is put into the other. These liquids are contained in glass tubes, drawn out at both ends into capillaries that make an obtuse angle with the wider part. The tubes are first weighed, then filled, closed before the blowpipe, and again weighed. They contain about 3 c.c. of liquid, pass readily through the narrow necks of the bottles, and can be broken by moderately shaking the bottles. Before this is done, however, the bottles are closed with their stoppers—smeared with deliquesced phosphoric acid to insure a perfect joint—and are placed in a water-bath of constant temperature. The T-tube is now connected with a two-necked Woulff's bottle, filled with coloured distilled water, and communicating by its second neck with an air-pump. Air is exhausted, until the pressure within the apparatus is diminished to an extent equivalent to the amount of tension to be expected from the vapours of the liquids, and the pinch-cock is then closed, so as to interrupt communication with the Woulff's bottle. The air-pump being disconnected, atmospheric pressure is restored in the Woulff's bottle, and on carefully opening the pinch-cock the water is allowed to ascend half way up the long tubes; the pinch-cock is then closed, and the Woulff's bottle removed. The apparatus is thus converted into a very delicate differential manometer, affording direct readings of the difference of pressure in the two bottles in terms of water centimetres; for convenience, the two tubes are brought closely together (see Figure) and a scale is placed behind them.

The apparatus is quite independent of changes in the atmospheric pressure; the change in capacity, caused on either side by an alteration in the level of the water in the tubes, is, moreover, so slight in proportion to the volume of air in the bottles, that it can safely be neglected; the effect of capillarity in the two tubes is equal and opposite, so that this too may be left out of account. There remains only the effect of the air left in the apparatus by the air-pump. It

is obvious that equilibrium being once established, and the temperature in all parts remaining the same, the pressure of the air in the one half will always counterbalance that in the other. In fact, partial exhaustion was only resorted to as a means of preventing too great an outward pressure during the course of the experiment, since it was difficult to prevent leakage where there was any outward pressure upon the stoppers. Partial exhaustion, besides obviating this difficulty, proved directly advantageous by promoting a more rapid diffusion of the vapours, and thereby shortening the duration of the observations.

The apparatus having been made ready, communication between the two halves was temporarily interrupted, and the tubes containing the liquids broken by shaking the two bottles simultaneously. After 10—15 minutes communication was restored, and now the level of the water in the two manometer tubes, equal before, was seen to differ considerably, indicating a higher pressure in the bottle containing the pure solvent. Readings being made from time to time, this difference of level sometimes appeared virtually constant for hours, whilst in other cases it would exhibit considerable variations, which I ascribe to slight inequalities of temperature and to the unequal concentration of the solution in different parts of its bottle. After standing 24 hours, the aqueous vapour from the manometer tubes generally began to diffuse into the bottles, and rendered further observations useless by moistening the ether or carbon bisulphide.

The readings give the difference between the vapour-tension of the pure solvent and that of the solution; that is, the depression of tension which corresponds with the proportion of iodine to solvent in the solution. To calculate the concentration of the solution at the moment of observation, I required two data: the amount of iodine and of solvent introduced into the bottle (which I obtained from the weighings of the sealed tubes and from the known strength of the solution with which they were filled); and secondly, the amount of solvent which had assumed the gaseous state, and must therefore be deducted from the original quantity in solution. This was easily calculated by the regular gasometric formula, the volume of gas being 270 c.c., the temperature being known, and the pressure being that of the vapour of the pure solvent, less the depression formed by the direct observation. I found that I could employ the vapour-tensions of pure ether and carbon bisulphide from tables calculated from Regnault's measurements, as a few direct comparisons proved that they agreed with those given by my apparatus, within the limits of experimental error. The expression for the amount of solvent remaining in the solution at the moment of observation is therefore—

$$a - \frac{270.w.(f-e)}{760(1+\alpha t)},$$

where a = grams of solvent originally present; f = the tension at the temperature t of the pure solvent, expressed in millimetres of mercury; e = the depression of tension, also in terms of millimetres of mercury; w = weight in grams of 1 c.c. of the vapour under standard conditions. Now if b = the weight of iodine in the solution, and p = the ratio of solvent to iodine—

I. $$p = \frac{b}{a - \frac{270.w.(f-e)}{760.(1+\alpha t)}}.$$

The concentration being thus ascertained, the calculation of the molecular weight of iodine was made according to the formula—

II. $$M_1 = M_0 \frac{p(f-e)}{e},$$

M_1 and M_0 being the molecular weights of iodine and solvent respectively. This is a working formula derived by Raoult from an expression for the relation between the ratio of molecules of solvent and substance dissolved on the one hand, and the ratio between the tension of the pure solvent and the depressed tension on the other, where the dissolved substance itself has a comparatively insignificant tension. It is interesting to note that the latter expression was reached independently and simultaneously by Planck, both papers having appeared in vol. i, No. 7 of the *Zeitschrift für physikalische Chemie*.

In the following tabulated statement of my observations, the first two columns show the weights of the ingredients of the solution originally introduced; the third gives the temperature; the fourth, the depression of tension; the fifth, the true tension of the solution; the sixth, the concentration as calculated by formula I; finally, we have the molecular weight as calculated by formula II. Before giving the results obtained for iodine, I think it useful to give a summary of a few test experiments made on the molecular weight of naphthalene, which not only proved the trustworthiness of the method, but also showed that there is no specific difference between ether and carbon bisulphide which could invalidate the effect of the great difference of the molecular weights found for iodine.

Naphthalene in Carbon Bisulphide.

a.	*b.*	*t.*	*e.*	*f* − *e.*	*p.*	M_1.	Average.
5·4082	0·2586	27·5°	9·47	377·09	5·18	129	132
—	—	27·5	10·93	375·65	5·18	135	

Naphthalene in Ethyl Ether.

a.	*b.*	*t.*	*e.*	*f* − *e.*	*p.*	M_1.	Average.
2·8359	0·1462	27·5°	21·12	557·27	6·53	127	127·5
—	—	27·5	21·08	557·31	6·53	128	
—	—	27·5	21·14	557·25	6·53	127	
—	—	27·5	21·17	557·22	6·53	128	

Average in CS_2..... $M_1 = 132$
Average in $C_4H_{10}O$ ..... $M_1 = 127·5$
Theory for $C_{10}H_8$ ..... $M_1 = 128$.

Iodine in Carbon Bisulphide.

a.	*b.*	*t.*	*e.*	*f* − *e.*	*p.*	M_1.	Average.
5·6528	0·4388	27·3°	9·72	373·92	8·37	239	264
—	—	27·3	8·59	375·05	8·37	278	
—	—	27·3	8·81	374·83	8·37	271	
—	—	27·3	9·08	374·56	8·37	268	
5·1862	0·4026	27·5	8·10	378·48	8·46	300·5	300·5
—	—	27·5	8·10	378·48	8·46	300·5	
5·4579	0·2594	27·5	4·60	381·98	5·15	324	320
—	—	27·5	4·51	382·07	5·15	332	
—	—	27·5	4·66	381·92	5·15	320	
—	—	27·5	4·76	381·82	5·15	314	
—	—	27·55	4·80	382·52	5·15	310	
4·9030	0·2330	27·5	4·67	381·91	5·20	326	326·5
—	—	27·5	4·60	381·98	5·20	327	

Total average..... $M_1 = 303·25 \pm 5·10$
Theory for I_2..... $M_1 = 254$
Theory for I_3..... $M_1 = 381$.

Iodine in Ethyl Ether.

a.	*b.*	*t.*	*e*	$f-e$.	*p.*	M_1.	Average.
3·2578	0·2546	27·2°	8·20	563·69	9·59	488	
—	—	27·2	7·50	564·39	9·59	534	
—	—	27·2	7·81	564·08	9·59	512	504·7
—	—	27·35	8·09	567·05	9·60	497	
—	—	27·3	8·16	565·90	9·60	492·5	
3·2864	0·2058	27·3	7·46	566·60	7·68	443	
—	—	27·3	4·84	569·22	7·68	653	577·2
—	—	27·3	5·04	569·02	7·68	642	
—	—	27·3	5·66	568·40	7·68	571	
3·6809	0·2305	27·4	6·51	569·72	7·50	486·5	
—	—	27·4	6·48	569·75	7·50	487	480·7
—	—	27·45	6·77	570·54	7·51	468·5	
3·4343	0·3151	27·5	6·99	571·40	7·62	461	
—	—	27·5	7·14	571·25	7·62	451	
—	—	27·5	6·43	571·96	7·62	501·5	466·1
—	—	27·5	7·14	571·25	7·62	451	

Total average ..... $M_1 = 507{\cdot}2 \pm 10{\cdot}5$
Theory for I_4 ..... $M_1 = 508$.

It seems very probable, therefore, that iodine in its red solutions has a molecular weight corresponding to I_4, whilst in the violet solution in carbon bisulphide there is a less complex aggregation, giving a value between I_2 and I_3. I may as well remark that the values for p in the ether solutions correspond approximately with the ratio of one iodine molecule in 100 molecules of the solutions; in the carbon bisulphide solutions, this ratio varies between 1 : 100 and 1 : 200. Whilst greater dilution might appear more advisable from a theoretical point of view, it offers an apparently insurmountable difficulty in practice. A glance at the formulæ used in the calculation shows that the value of e enters three times in such a manner that any error attached to it would be tripled. As e decreases with the concentration, it is evident that a greater dilution than that employed by me will soon bring e to a point where the chance errors of observation become proportionately very great. Hence I agree with Raoult when he says that the method of determining molecular weights by the depression of the freezing point is preferable to the method by vapour-tensions. But for the problem which immediately interested me I lacked a liquid which would solidify, and also dissolve iodine with a pure violet colour, benzene, for instance, giving a very

impure bluish-brown. Nevertheless I endeavoured to obtain what corroborative evidence I could by experimenting on the freezing points of iodine in acetic acid and in benzene, but was forced to give up the attempt by the very slight solubility of iodine in these menstrua at low temperatures; the molecular weight of iodine as calculated from various series of observations seemed to increase continuously with the concentration, so that there was no point in the narrow limits between extreme dilution and saturation at which the molecular weight would appear constant, and could be accepted as trustworthy. A paper published since then by Paternò and Nasini (*Ber.*, **21**, 2155) on this subject contains a few figures for the molecular weight of iodine in acetic acid and benzene solutions, but I am unable to draw any other inference from them than from my own.

LXVII.—*The Use of Aniline as an Absorbent of Cyanogen in Gas Analysis.*

By Morris Loeb.

In a paper published in the *Comptes Rendus*, **100**, 1005, some time ago, Jaquemin proposed the use of aniline as an absorbent for cyanogen in quantitative gas analysis, without however giving details of any experiments as to the trustworthiness of the method. The proposal is a surprising one, considering that hydrogen cyanide is always formed in the preparation of cyananiline; this fact is distinctly stated by Hofmann (*Annalen*, **66**, 129), who accounted for its production by certain secondary reactions which he studied. It is also to be noted that Jaquemin, in the same paper, describes a very satisfactory method of preparing cyanogen gas in the wet way, and that he probably employed the moist cyanogen in his experiments with aniline. As the presence of water seems to favour most of the reactions of cyanogen, there did not seem to be any conclusive evidence that dry cyanogen would be totally absorbed by aniline. At all events, it seemed worth while to make the experiment with cyanogen prepared in the old way, and at the same time to ascertain to what extent the development of hydrocyanic acid would interfere with Jaquemin's proposed method for gas analysis. For this purpose, cyanogen prepared from dry mercuric cyanide was brought into contact with recently distilled aniline. The gas was, indeed, absorbed rapidly and completely, nor did a bubble of gas appear after 24 hours' standing. But as soon as carbon dioxide was passed in, the presence

of hydrocyanic acid became apparent. It was expelled from the aniline by the carbon dioxide, and could now be recognised both by its odour and by the prussian blue reaction. At the same time a considerable quantity of carbon dioxide is absorbed by the aniline and must be held in solution, as chemical union is impossible under the circumstances. As the same is said to be the case with carbon monoxide, and these two gases are those which generally accompany cyanogen, I fail to see how aniline can be generally useful in determining the amount of cyanogen in a mixture, apart from the fact that hydrogen cyanide is produced in the reaction, and is itself very loosely attracted by aniline.

The experiments by which I satisfied myself of this were made last April, in the laboratory of the Physical Association of Frankfort-on-Main, to the director of which, Dr. B. Lepsius, I am very much indebted. The details of a few of the most important tests are given below.

I. 32·88 c.c. of cyanogen gas (under standard conditions) were absorbed immediately by 12·5 c.c. aniline; after 25 hours no trace of gas had been evolved.

II. A mixture of cyanogen and dry air was introduced into a U-shaped eudiometer, provided with stopcocks and filled with mercury. Aniline was first added and allowed to absorb the cyanogen, and dry carbon dioxide was then passed in; when no further change took place, the unabsorbed gas was transferred to a test-tube over mercury, and brought in contact with a few drops of sodic hydrate; the alkaline solution gave an appreciable test for hydrocyanic acid with ferrous and ferric salts. In the following table the measurements and the results are given:—

	t.	B.	c.c.	Corrected.	
Volume of cyanogen and air.....	19·0°	752·1	60	55·34	—
Volume 22 hours after introducing aniline.....	19·5	752·1	7·7	7·09	—
Volume of cyanogen absorbed....	—	—	—	—	48·25
After addition of carbon dioxide..	19·5	752·1	36·75	33·84	—
Volume carbon dioxide.....	—	—	—	—	26·75
After 23·5 hours.....	19·5	752·0	21·00	19·33	—
Volume carbon dioxide absorbed..	—	—	—	—	14·51

III. A similar experiment, performed in a somewhat different order, and with the use of a straight eudiometer, gave an analogous result. H = the height of the column of mercury, h = the height of the column of aniline reduced to mercury.

	t.	B.	H.	*h.*	c.c.	Corrected.
Volume of carbon dioxide.....	19·5°	752·1	—	—	56·5	52·03
Volume of carbon dioxide and cyanogen.....	19·5	752·1	—	—	108·5	99·91
Volume of cyanogen.....	—	—	—	—	—	47·88
Vol. 22 hours after introduction of aniline	19·5	752·0	227	5·3	43·0	27·32
Volume of gas absorbed	—	—	—	—	—	72·59

47·88 c.c. cyanogen gas and 24·71 c.c. carbon dioxide have, therefore been absorbed. In this case, too, the residual gas had a decided odour of prussic acid.

LXVIII.—*On two New Chlorides of Indium and on the Vapour-densities of Indium, Gallium, Iron, and Chromium.*

By L. F. Nilson and Otto Pettersson.

The decisive results for the trivalency of aluminium which we obtained in our researches on aluminium chloride (*Oefversigt af K. Wetenskaps Akad. förhandl.*, 1887, No. 8, and *Zeitschrift f. physikal. Chem.*, 1887, 459) rendered it most desirable that the earlier work on the molecular weights of the chlorides of other elements of the same group should be revised. At the conclusion of our communication, therefore, we invited those chemists who had previously worked in this direction to undertake this revision. In reply, we received a letter from Lecoq de Boisbaudran expressing the wish that we would undertake the work on gallium, and in the most obliging manner sending us a supply of pure material. Clemens Winkler wrote to the same effect in respect of indium and gallium, and at the same time placed at our disposal a quantity of these rare elements. With these materials and those already in our possession, we have undertaken the investigation. We would, however, observe that the amount of gallium in our possession, notwithstanding the liberality of the above-mentioned chemists, was insufficient to enable us to investigate the gallium chlorides as completely as we could have wished.

V. Meyer, who had already determined the vapour-density of the chlorides of iron, reserved to himself the right of revising the density of ferric chloride, and has recently published his results (Grünewald

and V. Meyer, *Ber.*, 1888, **21**, 687), but as he proposed to us that we should definitely ascertain the molecular weight of ferrous chloride, we were prompted to undertake some experiments on the latter.

It also seemed of interest to include the chromous and chromic chlorides in our researches, especially as these compounds, so far as we are aware, have not hitherto been examined in this respect.

As will be seen from the following account, several of our experiments were carried out in porcelain vessels at a temperature which was not accurately determined. The reason of this was that our platinum apparatus towards the conclusion of our work must have become slightly defective, the leak only becoming apparent at an intense heat and under pressure; the level of the mercury in the measuring tube or of the liquid in the manometer* no longer remaining constant, but slowly and gradually changing. As it had to be sent to Paris for repair, we could not delay the completion of our experiments until it was returned; and from this time forward all the experiments were conducted in porcelain vessels, the temperature being approximately estimated from our knowledge of the heat which the furnace was capable of giving.

Some of the estimations were made in the vapour of boiling mercury, sulphur, or stannous chloride, contained in tubes of hard Thüringen glass. By means of a Muencke five-light burner, it was easy to maintain the vapour of the mercury or sulphur at the desired height, if the tube were surrounded with asbestos cardboard. Stannous chloride on the contrary required strongly heating in a blowpipe flame; the bottom of the tube in fact appeared to be at a low red heat, although Grünewald and V. Meyer (*Ber.*, 1888, **21**, 22, and *Zeitschrift f. physikal. Chem.*, **2**, 184) state that it boils constantly at 606°, a temperature which the Thüringen glass stands well. If the substance contained in the bath is not allowed to cool or solidify, several experiments can be made one after another without any danger of breaking the tube. At the conclusion of the series of experiments, the substance is of course poured out of the bath while it is still liquid.

I. Chlorides of Indium.

Hitherto the only known chloride of indium is that whose composition is represented by the formula In_2Cl_6 or $InCl_3$. When the metal

* For the various details of the method of experimenting, and the mode of calculating the results, we must refer to our former paper on vapour-density determinations (*J. pr. Chem.*, 1886, [2], **33**, 1), and merely add here that the platinum apparatus we employed in the experiments in question had a capacity of 118·19 c.c. for the cylinder, which was 240 mm. high and 25 mm. in diameter, and 7·48 c.c. for the neck, which was 300 mm. high and about 5·6 mm. in diameter. That employed for the chromium chloride experiments had a cylinder of a capacity of 116·66 c.c.

is heated in chlorine, the latter being in excess, this chloride is obtained in beautiful, dazzling white plates, which at a temperature approaching redness volatilise without previously undergoing fusion.

Already in 1867 Clemens Winkler (*J. pr. Chem.*, **102**, 96), in his preliminary investigation of the indium compounds, noticed that the metal when exposed to a current of chlorine melts at first to a brown mass, but he did not further investigate this substance. He, however, expressed the opinion that it might possibly be a lower chloride of indium, corresponding with the suboxide which he had obtained as a black, pyrophoric powder on heating indium oxide at 300° in hydrogen.

We have found, however, that indium, in the state of vapour, gives three different, well-characterised chlorides, and now proceed to describe their mode of preparation, properties, and composition.

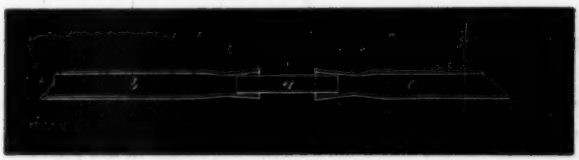
Indium Trichloride, $InCl_3$.—Metallic indium is not changed by exposure at the ordinary temperature to dry hydrogen chloride free from air, but if heated in a current of this gas the hitherto unknown dichloride, $InCl_2$ (see p. 818), is formed. If this is gently heated in a stream of chlorine, it is easily converted into the trichloride having all the properties ascribed to it by Clemens Winkler.

It is well known that, in the literature of the subject, only one vapour-density determination of this chloride occurs, namely, that made by V. and C. Meyer (*Ber.*, 1879, **12**, 611), in an appropriate furnace, using a tube of hard glass coated with clay and a temperature approaching a bright red heat; the density found was 7·87 instead of 7·584 for $InCl_3$. According to the authors, the formula of the chloride is thereby confirmed, and the trivalency of the element established. They describe their investigation as follows:—"Indium chloride is not volatile in the vapour of diphenyl perchloride, which boils far above 440°, and sublimes but slowly in boiling phosphorus pentasulphide (530°). At a low red heat, however, it sublimes easily but not very rapidly, and it is only at a bright red heat that it passes into the state of a normal gas. The supposition that indium chloride in the state of vapour is a mixture of Cl_2 and an unstable In_2Cl_4, is improbable, as indium does not form any derivatives corresponding with the ferrous compounds, but only one series like aluminium. No free chlorine could be detected in the apparatus after the experiment, the chloride being found quite unchanged in beautiful lustrous crystals."

As already pointed out, however, indium forms two new chlorides, not a dichloride only but also a monochloride, both of which are stable in the gaseous state, and as the existence of these then unknown chlorides renders futile the remark of the learned authors

above quoted, we felt it to be necessary to submit the indium trichloride to a renewed investigation.

In order to obtain material for the vapour-density determination, a quantity of indium dichloride sufficient for each experiment was first prepared by heating a weighed quantity of the metal in gaseous hydrogen chloride in a narrow drawn-out tube (see p. 818), the hydrogen evolved being collected as usual in a Schiff's apparatus. The dichloride thus formed was converted into the trichloride by heating it gently in dry chlorine free from air, and then sublimed into an adjacent portion of the tube in a stream of pure carbon dioxide, so as to remove any adhering free chlorine. A platinum tube about 20—25 mm. long was then inserted in the end of the tube, which must be drawn out as shown in the figure. The little platinum tube, *a*, thus



forms a connection between the ends of the two tubes *b* and *c*. By continued and careful turning of the platinum in the drawn-out openings of the glass tubes, it may without difficulty be made to fit quite air-tight. If the glass tubes are carefully drawn out, perfectly cylindrical, and the openings but slightly conical, the platinum tube remains quite firm even when the chloride is sublimed into it; this is effected in a stream of carbon dioxide, and as the platinum readily cools, the chloride, although so volatile, condenses almost entirely in the metal tube. As soon as this is cold, the chloride is turned into a little cup by means of a pair of tongs. The empty platinum tube is then weighed and also the little cup filled with chloride and inclosed in watch-glasses; in this way the weight of substance to be employed is known, which in our experiments corresponded very nearly with the weighed quantity of metal taken.

The calculated vapour-density* of the chloride $InCl_3$ is 7·548.

Experiment 1 (see Table I, p. 818) in sulphur vapour gave only a minimal vaporisation not measurable volumetrically. At the conclusion of the experiment, however, we observed on the sides of the glass tube several beautifully iridescent, well-formed crystals of the chloride as thin six-sided plates.

We can therefore confirm the statement of V. and C. Meyer, that

* The Meyer-Seubert atomic weights are used in all the calculations in this memoir.

TABLE I.—*Vapour-density of Indium Trichloride.*

Expt.	Temperature determination.			Vapour-density determination.			Remarks.
	Vol. of gas expelled. c.c.	Temp. of the measuring tube.	Calculated temperature of expt.	Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0° and 760 mm.	Vapour-density found.	
1	—	—	440°[1]	—	—	—	Minimal vaporisation.
2	—	15·8°	606°[2]	0·0635	6·022	8·156	Slow vaporisation.
3	92·984	14·0	850	0·0671	7·021	7·391	Rapid volatilisation.
4	98·165	14·8	1048	0·0560	6·447	6·716	
5	—	13·1	1100–1200°[3]	0·0573	7·110	6·234	

[1] In sulphur vapour. [2] In stannous chloride vapour. [3] The exact temperature could not be determined on account of a defect in the platinum apparatus, but it was evidently higher than in Experiment 4.

at 440° indium trichloride does not appreciably vaporise, and that at a temperature which, according to our experiments lies between 606° and 850°, its vapour-density corresponds with the value 7·548 calculated from the formula $InCl_3$. In boiling stannous chloride, its vapour-density is somewhat higher; as, however, it volatilises but slowly at this temperature, it is improbable that there is any lower temperature at which an indium chloride of vapour-density 15·168, corresponding with the formula In_2Cl_6, can actually exist in the gaseous state. At temperatures above 850°, indium trichloride, as the values we found show, undergoes a progressive dissociation probably into lower chlorine compounds and free chlorine.

Indium Dichloride, $InCl_2$.—If indium is heated to its fusion point in a current of dry hydrogen chloride free from air, it yields indium dichloride with evolution of hydrogen; at first, indeed, a reddish-brown liquid is formed containing indium monochloride (p. 820), but this, as soon as the hydrogen chloride is in excess, gradually becomes lighter and lighter, and ultimately of a pure amber colour. It then consists of the pure dichloride, and on cooling solidifies to a white radiated crystalline mass which if strongly heated volatilises, and is deposited close to the flame in colourless needles. Any adhering hydrogen chloride may be removed by distillation in a current of dry carbon dioxide free from air. On exposure to moist air, it deliquesces,

but it remains unchanged in dry air. Water decomposes the chloride with a reddish sheen (from monochloride formed as an intermediate product?) into trichloride which remains dissolved and metallic indium which is deposited as a grey spongy mass; the latter acquires metallic lustre when consolidated to a lump by means of a glass rod. The dichloride, therefore, cannot exist in aqueous solution, but is decomposed with formation of the trichloride; the reaction being—

$$3InCl_2 = 2InCl_3 + In.$$

The amount of metal we obtained on treating the dichloride with water is somewhat less than that required by the equation, which is doubtless to be ascribed to the formation of some oxychloride from the oxygen present.

The composition of the new chloride is shown by the following syntheses and analysis.

Synthesis I.—0·0573 gram of metallic indium treated as above gave the following quantities of hydrogen at 0° and 760 mm.:—

	Found.		Calculated.	
	c.c.	gram.	c.c.	gram.
Hydrogen...	11·04	0·000988	11·28	0·001010

From this weighed quantity of metallic indium, 0·0904 gram of indium dichloride was sublimed into the platinum cup, and used for Experiment 3, the calculated yield being 0·0929 gram $InCl_2$ supposing none of the chloride to have been lost.

Synthesis II.—0·0966 gram of metallic indium gave—

	Found.		Calculated.	
	c.c.	gram.	c.c.	gram.
Hydrogen...	18·60	0·001665	19·02	0·001703

Synthesis III.—0·1203 gram of metallic indium gave 0·1940 gram of dichloride, which was used in the following analysis; the calculated yield should have been 0·1964 gram.

Analysis.—0·1940 gram of indium dichloride was treated with boiled water. The solution yielded 0·3013 gram of silver chloride, corresponding with 0·07451 gram of chlorine; and 0·1008 gram of indium oxide corresponding with 0·0832 gram of indium. The metallic indium which separated weighed 0·0374 gram. Expressed centesimally, the results are—

	Found.		Calculated.	
Residual metallic indium..	19·28	62·16	20·53	61·58
Indium as oxide in solution	42·88		41·05	
Chlorine.....		38·41		38·42
		100·57		100·00

TABLE II.—*Vapour-density of Indium Dichloride.*

Expt.	Temperature determination.			Vapour-density determination.			Remarks.
	Vol. of gas expelled. c.c.	Temp. of the measuring tube.	Calculated temperature of expt.	Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0° and 760 mm.	Vapour-density found.	
1	96·440	15·2°	958°	0·0592	5·965	7·675	In platinum
2	100·608	15·8	1167	0·0719	8·496	6·545	cylinder.
3	—	—	1300-1400	0·0904	10·865	6·435	In porcelain.

The calculated vapour-density of the chloride $InCl_3 = 6·362$.

Indium dichloride, which is incapable of existing in aqueous solution, is a very stable compound at high temperatures. At 958°, the vapour-density found is somewhat higher than is required by the formula $InCl_2$, but at higher temperatures it is quite normal.

Indium Monochloride, InCl.—The circumstance that metallic indium when gently heated in gaseous hydrogen chloride, the metal being in excess, forms a dark-red liquid, led us to believe in the existence of a lower chloride, probably identical with the product noticed by Clemens Winkler on treating the metal with chlorine, but which he did not examine.

In order to obtain this in a state of purity, a weighed quantity of indium was converted into the dichloride, which was then distilled in a current of carbon dioxide into a neighbouring portion of the glass tube, where a weighed quantity of the metal somewhat larger than the first had been already placed; the small tube was then fused off on both sides of it. On heating this tube in the naked flame, reaction set in, the liquid becoming blood-red, and forming numerous drops like bromine which adhered to the glass. On cooling, these solidified to vitreous or radiated masses somewhat resembling hæmatite in appearance. The slight excess of metallic indium employed remained as a small button after the chloride had been volatilised in a current

of carbon dioxide, as will be seen in the synthesis described hereafter.

In thin layers, the new chloride when melted is a liquid of a beautiful red, in thicker layers it is almost black. It soon attracts moisture from the air, deliquesces, and decomposes gradually into indium trichloride and metallic indium, becoming grey in consequence. The monochloride is at once decomposed by water into the trichloride and metal, the reaction doubtless taking place according to the following equation:—

$$3InCl = InCl_3 + In_2,$$

the same remarks applying as in the case of the similar decomposition of indium dichloride.

Synthesis.—0·1100 gram of metallic indium was heated in gaseous hydrogen chloride to convert it into the dichloride. When this had acted on 0·1160 gram of indium in an atmosphere of carbon dioxide in a sealed tube, the red chloride formed was distilled off, leaving a metallic button which weighed 0·0050 gram instead of 0·0060 gram. Now 0·2200 gram of indium should yield 0·2886 gram of indium monochloride; and, in fact, 0·2741 gram of this chloride was obtained. The difference represents the loss occasioned by the distillation.

Analysis.—0·1656 gram of indium monochloride after decomposition with boiled water gave in the solution 0·1606 gram of silver chloride corresponding with 0·0397 gram of chlorine, and 0·0575 gram of indium oxide corresponding with 0·04746 gram of indium. The metallic indium which separated weighed 0·0790 gram. Expressed centesimally, the results are—

Residual metallic indium..	47·71	76·33	50·82	76·23
Indium as oxide in solution	28·62		25·41	
Chlorine.....		23·98		23·77
		100·31		100·00

TABLE III.—*Vapour-density of Indium Monochloride.*

Experiment.	Temperature employed.	Vapour-density determination.			Remarks.
		Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0° and 760 mm.	Vapour-density found.	
1	1300—1400°	0·0660	9·224	5·534	In porcelain.
2	1100—1150	0·0536	7·826	5·296	
3	1200—1300	0·0549	7·894	5·377	

The calculated vapour-density of the chloride InCl = 5·140.

The substance employed in Experiment 1 was not prepared in a sealed tube in the manner above described, but by the repeated distillation of the dichloride over metallic indium in a current of carbon dioxide. This sample consequently in all probability contained some unchanged dichloride, which accounts for the vapour-density found being somewhat too high.

The vapour-density determinations given above place it beyond doubt that the monochloride, dichloride, and trichloride of indium exist as definite compounds. The manner in which they are decomposed by water is also of especial interest, for with the exception of the lower chloride of gold, there is scarcely an instance known in which a chloride is decomposed by water with separation of the metal, and formation of a higher chloride. This behaviour of indium monochloride and dichloride shows us that indium in its soluble compound is decidedly and exclusively a trivalent element, although it is capable of existing in combination at a high temperature as a univalent or bivalent element.

Chlorides of Gallium.

Lecoq de Boisbaudran (Wurtz, *Dictionnaire de Chimie*, Article "Gallium" by Lecoq de Boisbaudran), the discoverer of this element, has pointed out the existence of two different chlorides of gallium. He is inclined to regard the higher chloride as gallium hexachloride, Ga_2Cl_6, and the lower as gallium dichloride, $GaCl_2$, in accordance with the views held at the time of his discovery as to the constitution of the iron chlorides and of aluminium chloride. The vapour-density determinations which he made by Dumas' method with the higher chloride seemed also to confirm the composition assigned to it. After the introduction of the air displacement method, however, Friedel obtained values which indicated that this formula should be halved.

Lecoq de Boisbaudran.	13·4 at 247°	boiling point 215—220°.
	11·9 „ 273	
	10·0 „ 350	
Friedel	7·8 „ 440	
	8·5 „ 350	
	6·6 „ 440	

The calculated vapour-density for Ga_2Cl_6 = 12·16, that for $GaCl_2$ = 6·08. In order to place us in a position to decide on the true formula of this chloride, Lecoq de Boisbaudran placed at our disposal the necessary material. As the vapour-density of the lower gallium

chloride is quite unknown, we have also instituted a couple of experiments with it.

Gallium Trichloride, $GaCl_3$.—Like aluminium, but unlike indium, metallic gallium yields the trichloride when it is heated in gaseous hydrogen chloride. The reaction takes place at a gentle heat; but at the ordinary temperature the metal remains quite unchanged if the gas is dry and free from air. If warmed, a highly refractive liquid is formed with evolution of hydrogen, and if more strongly heated this volatilises and is deposited in the tube close to the flame in long, needle-shaped crystals: the metal is completely converted into the chloride, and leaves no residue. As soon, however, as the product is distilled in a current of carbon dioxide to free it from adhering hydrogen chloride, a trace of a brownish-yellow, slightly volatile residue is noticed in the tube; this instantly becomes colourless in gaseous hydrogen chloride. This appearance, we believe, can scarcely be ascribed to impurity in the metal employed, but should more probably be regarded as due to a lower chloride corresponding with indium monochloride.

Lecoq de Boisbaudran, on treating gallium dichloride with much water, obtained a brown subtance, which if left under water evolved gas slowly, and rapidly if dissolved in hydrochloric acid. This compound, which was not analysed, he regarded as in all probability a lower oxide of gallium. We are of opinion, however, that it was perhaps the monochloride of gallium, which might be formed in the following way—

$$2GaCl_2 = GaCl_3 + GaCl,$$

and may be identical with the brownish-yellow substance which is formed in small quantity in the preparation of gallium dichloride (p. 824). Its true nature, however, must remain an open question until larger quantities have been obtained.

Synthesis of Gallium Trichloride.—In two experiments, metallic gallium gave the following results when heated in dry hydrogen chloride free from air:—

Hydrogen at 0° and 760 mm.

Experiment.	Weight of metal.	Hydrogen.	
		Found.	Calculated.
1	0·0236 gram.	11·57 c.c. 0·001036 gram.	11·30 c.c. 0·001012 gram.
2	0·0220 „	10·86 „ 0·000973 „	10·54 „ 0·000944 „

TABLE IV.—*Vapour-density of Gallium Trichloride.*

Experiment.	Temperature employed.	Vapour-density determination.			Remarks.
		Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0° and 760 mm.	Vapour-density found.	
1	350°	0·0543	4·748	8·846	In mercury vapour.
2	440	0·0521	6·585	6·118	In sulphur „
3	606	0·0562	7·074	6·144	In stannous chloride vapour.
4	1000—1100	0·0567	8·457	5·185	In furnace with platinum vessel.

The vapour-density calculated on the formula $GaCl_3$ is = 6·081.

If our determinations are compared with the earlier ones, it is instructive to observe that gallium trichloride, like beryllium chloride, aluminium chloride, &c., has a vapour-density higher than the normal at the lowest temperature employed; but even at 440°, it has the normal value and retains it also at 606° in the vapour of stannous chloride; at still higher temperatures, it suffers dissociation like many other trichlorides. The difference in the values obtained by Lecoq de Boisbaudran and Friedel at one and the same temperature must be set down to the different methods employed by the two investigators.

Gallium Dichloride, $GaCl_2$.—According to Lecoq de Boisbaudran this compound may be obtained by heating the metal in chlorine, taking care to keep the gallium in excess. We preferred, however, to prepare it from weighed quantities of the metal in exactly the same way as indium monochloride.

We allowed 0·0352 gram of gallium to act on the trichloride formed from 0·0170 gram of gallium, a quantity more than sufficient to convert it into dichloride, or even into monochloride. After long-continued heating and completion of the reaction, we opened the tube and distilled out the colourless chloride in a stream of carbon dioxide, a button of gallium being left which weighed 0·0225 gram. The trichloride consequently had taken up 0·0127 gram of gallium, or 0·0042 gram more of the metal than corresponds with the formula $GaCl_2$. We noticed, however, not only that several exceedingly minute globules of gallium remained in the tube and could not be extracted, but also that the tube was covered with a thin coating of the brownish-yellow substance previously mentioned when speaking

of the trichloride; this we are inclined to regard as a rather unstable gallium monochloride, as on exposure to an atmosphere of hydrogen chloride or chlorine it instantaneously becomes white, and is converted into colourless drops which solidify to a crystalline mass on cooling, volatilise when heated, and, in short, exhibit all the properties of gallium trichloride.

Gallium dichloride, when melted, forms a limpid refractive liquid which on cooling solidifies and becomes crystalline; it distils when heated, and is deposited on the tube near the flame in a solid state. Its vapour, like that of the trichloride, fumes in the air on account of its attraction for the moisture in it.

TABLE V.—*Vapour-density of Gallium Dichloride.*

Experiment.	Temperature employed.	Vapour-density determination.			Remarks.
		Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0°, and 760 mm.	Vapour-density found.	
1	1000—1100°	0·0402	6·450	4·823	In porcelain.
2	1300—1400	0·0464	10·060	3·568	

The theoretical vapour-density of the chloride $GaCl_2$ is = 4·859.

Gallium dichloride does not appear to be so stable as indium dichloride at a high temperature. Experiment 2 shows that it is decomposed at a full white heat, which is most probably to be attributed to the formation of a gallium monochloride and free chlorine. According to our experience, dissociation of a chloride with increase of temperature only takes place when a lower chloride exists which is more stable at the higher temperature. For example, in our experiments with beryllium chloride, indium monochloride, ferrous chloride, &c., we always obtained values corresponding with those calculated, however high the temperature might be; whilst all the chlorides we have examined of which lower chlorine compounds exist gave, at the highest temperatures, values considerably lower than the theoretical.

Remarks on the Valency of the Elements of the Aluminium Group.

The elements of the third group whose chlorides we have already examined give the following chlorine compounds:—

	Monochloride.	Dichloride.	Trichloride.
Aluminium..	Wanting	Wanting	$AlCl_3$, colourless, infusible at the ordinary pressure, crystalline.
Gallium	Not known for certainty	$GaCl_2$, colourless, fusible, crystalline	$GaCl_3$, colourless, fusible, crystalline.
Indium	InCl, reddish-yellow, when fused reddish-brown	$InCl_2$, colourless, when melted amber-yellow	$InCl_3$, colourless, infusible, crystalline plates.

It is noteworthy that aluminium, when treated with hydrogen chloride, displaces 3 atoms of hydrogen, indium 2 atoms, and thallium (according to Lepsius, *Ber.*, 1888, **21**, 556) 1 atom. In this group, also, there is a decided tendency to form a larger number of chlorine compounds as the atomic weight increases. Aluminium forms but 1 chloride, whilst gallium yields 2, indium 3, and thallium 4 chlorides, TlCl, Tl_2Cl_3, $TlCl_2$, and $TlCl_3$.

The question, which is so interesting theoretically, as to whether aluminium behaves towards chlorine exclusively as a triad, has already been touched upon by some French experimentalists. In researches on the action of aluminium trichloride on metallic aluminium at various temperatures, high and low, instituted by Troost and Hautefeuille (*Compt. rend.*, 1885, **100**, 1221), Hautefeuille and Perrey (*ibid.*, 1885, **100**, 1220), and Friedel and Roux (*ibid.*, 1885, **100**, 1191), it has been shown that a grey coating is formed on the metal, or a lustrous deposit on the sides of the tube. The origin of these substances, however, must be assigned to the presence of traces of silicon, as silicon could be detected in all, or, at least, in most instances. Friedel and Roux, indeed, state that when metallic aluminium is acted on by silicon chloride at a red heat it yields aluminium chloride with separation of silicon.

In order to settle this question, we prepared aluminium trichloride from a weighed quantity of aluminium by heating it in gaseous hydrogen chloride, and then allowed it to act on a weighed quantity of very thin aluminium foil in an atmosphere of carbon dioxide in a sealed tube which was heated over a bare flame. By long-continued action of the chloride, which under the high pressure fused to a limpid liquid, the aluminium foil did indeed become superficially of a greyish colour, but it was otherwise unchanged. If one end of the short tube was now heated, the chloride condensed in the other colder end in beautiful, well-defined, six-sided tables, identical in appearance with the crystals of indium trichloride. At the close of the experiment when all the chloride had sublimed to the other end

of the tube, the latter was opened, and the residual aluminium foil with adhering traces of aluminium chloride taken out and thrown into water, when after a momentary evolution of gas it completely regained its metallic lustre; on drying and weighing, it was found to have diminished in weight by a few tenths of a milligram only.

This inconsiderable loss is, moreover, easily explained by the action of traces of silicon chloride on the aluminium foil, forming aluminium chloride and silicide of aluminium which gave the grey appearance to the foil.

There is no reason to believe, therefore, in the existence of any chloride of aluminium lower than $AlCl_3$; Friedel and Roux indeed (*loc. cit.*) are inclined to regard the amount of chlorine in the above-mentioned grey coating as evidence that a second chloride of aluminium may be found, but as Hautefeuille and Perrey have shown that various oxychlorides of aluminium are formed when a mixture of chloride of aluminium and oxygen is passed over the heated metal, the low chlorine found may be due to oxygen not having been completely excluded in Friedel and Roux's experiments. Moreover, the vapour-density of aluminium trichloride as determined by us at various temperatures (*loc. cit.*, see also the remarks under *Gallium Dichloride*, p. 825), is evidence of the non-existence of a lower chloride of this element.

IV. Ferrous Chloride.

V. Meyer (*Ber.*, 1879, **12**, 1193, and 1884, **17**, 1335) has made vapour-density determinations of ferrous chloride under various conditions both in an atmosphere of nitrogen and also in hydrogen chloride. In the last series of experiments, he obtained the numbers 6·38 and 6·67, which are almost intermediate between those required by the formulæ Fe_2Cl_4 and $FeCl_2$, namely, 8·750 and 4·375. The substance evaporates rapidly at a yellow heat, and the results of the two experiments agree very well. The values found, therefore, seemed to the experimenter to indicate that at low temperatures the molecule of ferrous chloride had the formula Fe_2Cl_4, and that as the temperature rose it decomposed into $FeCl_2$; the temperature employed, however, was not high enough to enable him to obtain values corresponding with the latter. V. Meyer considered it necessary that the question should be further investigated, using platinum vessels, especially as the experiments with beryllium chloride have brought to light the disturbing influence involved in the use of glass or porcelain vessels; he has himself stated, however, that the glass tube in which the ferrous chloride was sublimed was not at all acted on.

As at V. Meyer's suggestion we have undertaken to renew the

investigation of this question, we deemed it before all things necessary to determine whether there was really a definite limit to the vapour-density of ferrous chloride at high temperatures. In the two experiments described below, made under somewhat different conditions, we obtained results which not only agreed with one another, but are in accordance with the values reckoned for the formula $FeCl_2$ to the second decimal place, and we therefore regard the question of the constitution of ferrous chloride as resolved, in so far as that the vapour of this substance at lower temperatures has a complex constitution, as shown by V. Meyer's determinations, and by analogy with what has been found to be the case with almost all the chlorides we have investigated, chloride of beryllium and chloride of aluminium for example, whilst at a white heat this decomposes, yielding a molecule of the normal composition $FeCl_2$.

In our vapour-density determinations, we used vessels of Bayeux porcelain, as like V. Meyer we found that the vapour of the chloride during its preparation and sublimation did not act on glass. After the experiment, we found that the substance dissolved in water as ferrous chloride without leaving any residue.

The substance was prepared by strongly heating soft iron wire in a platinum tube in a current of gaseous hydrogen chloride; the ferrous chloride formed was deposited in the fore part of the platinum tube close to the flame, as a radiated crystalline mass of the colour of siderite, and was as usual enclosed in a platinum cup for the experiment.

TABLE VI.—*Vapour-density of Ferrous Chloride.*

Experiment.	Temperature employed.	Vapour-density determination.			Remarks.
		Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0°, and 760 mm.	Vapour-density found.	
1	1300—1400°	0·0428	7·611	4·340	In porcelain.
2	1400—1500	0·0388	6·922	4·292	

The theoretical vapour-density required by the formula $FeCl_2$ is 4·375.

V. Chlorides of Chromium.

As is known chromium forms two compounds with chlorine, to which the composition represented by the formulæ Cr_2Cl_6 and $CrCl_2$

has hitherto been assigned, as in the case of the corresponding iron chlorides. The vapour-density of neither of these has been determined, and it seemed to us a matter of no small interest to examine these along with the chlorides of indium, gallium, and iron.

Chromium Trichloride, $CrCl_3$.—At the last "Naturforscherversammlung" in Wiesbaden, we noticed the splendid exhibit of Herr H. Deibel of various chemical preparations, amongst which was some resublimed chromium chloride in beautiful crystalline plates. This was obtained from him for the purpose of making the vapour-density determinations, and it gives us pleasure to testify to the purity of the specimen, as established by the reduction experiment described on p. 830. The chromium chloride, from exposure to the air, contained a little hygroscopic moisture, but this was removed by gently heating it in dry carbon dioxide free from air before weighing it out for the vapour-density determination. When the platinum cylinder was used in the determination, the chromium trichloride was placed in a small platinum cup; in the experiments with the porcelain vessel, a piece of a pipe stem was employed, which was made into a convenient shape before ignition in the blowpipe flame, the one end being closed by a kaolin stopper.

TABLE VII.—*Vapour-density of Chromium Trichloride.*

Expt.	Temperature determination.			Vapour-density determination.			Remarks.
	Vol. of gas displaced.	Temperature of measuring tube.	Calculated temperature.	Weight of chloride in grams.	Vol. of gas displaced, c.c. at 0° & 760 mm.	Vapour-density found.	
1	95·802	9·1°	1065°	0·0864	10·890	6·135	In platinum, volatilisation slow.
2	98·888	13·6	1191	0·0859	12·049	5·517	In platinum, volatilisation normal.
3	98·824	9·8	1277	0·0882	12·581	5·421	
4	101·420	14·6	1347	0·0791	12·670	4·827	
5	—	—	1100—1200	0·0578	7·890	5·670	In porcelain.
6	—	—	1250—1350	0·0498	7·440	5·177	
7	—	—	1350—1400	0·0638	10·770	4·580	

The theoretical vapour-density of the chloride $CrCl_3$ is 5·478. Chromium chloride, therefore, according to the determination made at 1200—1300°, has a vapour-density corresponding exactly with the formula of a trichloride. As vaporisation takes place but slowly at

1065°, when the value found is somewhat too high, there is probably no lower temperature at which a chloride of the hitherto accepted formula Cr_2Cl_6 and vapour-density 10·956 can exist in the gaseous state. At temperatures above 1300°, the chloride gave numbers somewhat too low, which was to be expected from the dissociation of the trichloride into free chlorine and the dichloride, which is stable at high temperatures.

Chromium Dichloride, $CrCl_2$.—This compound was prepared by the reduction of the trichloride with pure and dry hydrogen, at a temperature so low that the glass tube was not visibly red hot.

Reduction Experiment.—0·2927 gram of chromium trichloride gave 0·2274 gram of dichloride, a quantity which corresponds accurately with the theoretical.

The dichloride employed in the following vapour-density determination was prepared separately for each experiment, by introducing a weighed quantity of dry chromium trichloride into a porcelain or platinum cup, and reducing it in a stream of hydrogen, until hydrogen chloride could no longer be detected in the gas issuing from the mercury seal of the apparatus; the cup was then introduced as quickly as possible into a pair of watch-glasses, and weighed. In this way, a residue was obtained which always corresponded very accurately with the theoretical. The dichloride prepared in the manner described was white with a greyish shade, and volatilised with greater difficulty than any of the metallic chlorides we have examined. It vaporises rather slowly even in the most intense heat of the furnace we could obtain, using a Rohrbeck-Luhme 16-fold blowpipe lamp worked with gas and air at 2 atmospheres pressure.

TABLE VIII.—*Vapour-density of Chromium Dichloride.*

Experiment.	Temperature employed.	Vapour-density determination.			Remarks.
		Weight of chlorine in grams.	Vol. of gas displaced, c.c. at 0° and 760 mm.	Vapour-density found.	
1	1300—1400°	0·0545	5·403	7·800	In porcelain.
2	1400—1500	0·0561	5·960	7·278	
3	1500—1600	0·0551	6·847	6·224	

The theoretical vapour-density of the chloride $CrCl_2$ is 4·256. Thus we have found the vapour-density of chromous chloride to be

considerably higher than that required by the formula $CrCl_2$, but as the three experiments we made show a constant decrease of density with increase of temperature, there can be no doubt that chromous chloride in respect of vapour-density is strictly analogous to ferrous chloride, except that it volatilises at a much higher temperature, and scarcely becomes completely gaseous even at the highest heat attainable.

LXIX.—*On some Derivatives of Anthraquinone.*

By A. G. Perkin and W. H. Perkin, Jun., Ph.D.

In a previous paper on this subject, which we had the honour of communicating to the Society some time since (Trans., 1885, **47**, 679), we described a series of experiments on the products of the destructive distillation of sodium anthraquinonemonosulphonate.

This salt, when heated in an iron tube, yielded a brownish-red distillate, which on examination was found to contain metahydroxyanthraquinone, anthraquinone, and a peculiar red substance, which after purification by recrystallisation gave numbers agreeing with the formula $C_{28}H_{14}O_6$; it is nearly insoluble in all the usual solvents, and, curiously enough, in alkalis also.

On oxidation with chromic acid, it yields a white crystalline substance of the formula $C_{14}H_8O_4$, and when distilled with zinc-dust anthracene is produced, proving the substance to be an anthracene-derivative. The remarkable character of this decomposition of sodium anthraquinonemonosulphonate, has led us to continue our experiments, with a view to obtain some clue as to the constitution of the compound $C_{28}H_{14}O_6$. The extreme difficulty, however, of obtaining it in any quantity, owing to the tediousness of its preparation and purification, has prevented us from making as thorough an examination of the subject as we could have wished. We hope at some future date to be able to complete these experiments, and to establish without doubt the constitution of these derivatives.

Before proceeding with the examination of the red substance $C_{28}H_{14}O_6$, we thought it advisable to again analyse it, in order that there might be no doubt as to its formula. A quantity was therefore prepared and very carefully purified by repeated recrystallisations from glacial acetic acid. The pure substance was thus obtained as an orange, satiny, crystalline mass, which after careful drying at 110—120° gave the following results on analysis:—

0·1609 gram substance gave 0·0495 gram H_2O and 0·4450 gram CO_2.

	Theory. $C_{28}H_{14}O_6$.	Found.
C.....	75·34 per cent.	75·37 per cent.
H.....	3·14 „	3·42 „
O.....	21·52 „	21·21 „

If a hot dilute solution of this substance in glacial acetic acid is slowly cooled, groups of small, orange-coloured crystals separate, just visible to the naked eye; these when collected, washed, and dried, present the appearance of beautiful, satiny, orange-coloured flakes. If hot saturated solutions are rapidly cooled, the substance is deposited as an orange-coloured gelatinous mass.

In the previous paper it was stated that this compound, $C_{28}H_{14}O_6$, was converted into alizarin on fusion with potash. As it was important to be quite sure of this, the experiment was repeated with somewhat larger quantities, the decomposition being conducted in the following manner:—About 2 grams of $C_{28}H_{14}O_6$ were heated with a very concentrated solution of caustic potash at 180° for about 12 hours in a closed iron tube. The contents of the tube, which in appearance very much resembled an ordinary alizarin melt, were extracted with boiling water, the violet-coloured solution filtered from a small quantity of insoluble matter, and a little slaked lime added. The alizarate of lime thus precipitated was collected, well washed, suspended in water, decomposed with a little dilute hydrochloric acid, and the orange precipitate obtained was purified by recrystallisation from benzene. The product consisted of red needles melting at about 285°, and showing all the properties of alizarin. On analysis it gave the following numbers:—

0·1107 gram substance gave 0·0396 gram H_2O and 0·2821 gram CO_2.

	Theory. $C_{14}H_8O_4$.	Found.
C.....	70·00 per cent.	69·50 per cent.
H.....	3·33 „	3·97 „
O.....	26·66 „	26·53 „

The filtrate from the alizarate of lime was of a reddish colour, with a green fluorescence; on treatment with hydrochloric acid, it deposited a very small quantity of a nearly white precipitate, which when washed on a filter changed to a dirty green. On fusion with potash and treatment of the fused mass with water, a solution was obtained having all the properties of potassic alizarate.

This substance is therefore intermediate between the red substance and alizarin; it is probably identical with a substance, $C_{28}H_{14}O_7$, which

will be described later on, under the heading "Action of Nitric Acid on $C_{28}H_{14}O_6$." When fused with potash, $C_{28}H_{14}O_6$ is probably first oxidised to $C_{28}H_{14}O_7$, which then takes up the elements of water, and is converted into alizarin, thus :—

$$C_{28}H_{14}O_7 + H_2O = 2C_{14}H_8O_4.$$

That such a change really takes place is all the more probable, from the fact that the substance $C_{28}H_{14}O_7$, when fused with potash, also gives alizarin.

The residue from the fusion, insoluble in water, was crystallised from acetic acid, and thus obtained in orange needles, which were found to consist of unchanged $C_{28}H_{14}O_6$.

0·1491 gram substance gave 0·0470 gram H_2O and 0·4097 gram CO_2.

	Theory. $C_{28}H_{14}O_6$.	Found.
C.....	75·34 per cent.	75·01 per cent.
H.....	3·14 „	3·50 „
O.....	21·52 „	21·49 „

Action of Sulphuric Acid on $C_{28}H_{14}O_6$.

Cold Nordhausen sulphuric acid dissolves the red substance, forming a dirty green solution, which in contact with the air absorbs moisture, and deposits the unchanged substance as a transparent jelly. When the solution in Nordhausen acid is heated to 190°, the colour gradually changes to a brownish-red, and if at the end of about half an hour the mixture is poured into water, it dissolves to a clear solution, which on cooling sets to an opaque jelly. All attempts to free this mixture from sulphuric acid by treatment with the carbonates of lead or barium failed, owing to the salts of the sulphonic acid being insoluble.

If the mixture of the sulphonic acid and sulphuric acid is neutralised with potash and slowly evaporated, the dark solution deposits a small quantity of a crystalline salt, which under the microscope is seen to consist of long needles; these when heated to 100° fuse to a gummy mass. Fused with strong potash in an iron tube for some hours, and then decomposed with hydrochloric acid, a substance is obtained, which dyes mordanted cloth shades intermediate between those produced by anthrapurpurin and flavopurpurin.

Action of Nitric Acid on $C_{28}H_{14}O_6$.

On gradually adding the red substance, $C_{28}H_{14}O_6$, to cold fuming nitric acid of sp. gr. 1·5, it dissolves without evolution of red fumes,

forming a bromine-coloured solution. In examining the product of this reaction, the mass was allowed to stand for a short time, and then diluted with water. This caused the precipitation of a yellowish-white, amorphous substance, which was filtered off, well washed, and dried. It was then dissolved in a little hot aniline or nitrobenzene, filtered, and boiling alcohol added drop by drop to the hot solution until the mixture showed a tendency to become milky. On allowing this to cool slowly, minute crystals were deposited, which, after collecting, washing with alcohol, and drying at 110°, gave the following numbers on analysis:—

I. 0·1366 gram substance gave 0·0418 gram H_2O and 0·3658 gram CO_2.

II. 0·1650 gram substance gave 0·0505 gram H_2O and 0·4420 gram CO_2.

	Theory. $C_{28}H_{14}O_7$.	Found. I.	Found. II.
C	72·72 p. c.	73·01	73·05 p. c.
H	3·03 „	3·40	3·40 „
O	24·24 „	23·59	23·55 „

This substance has therefore the formula $C_{28}H_{14}O_7$, being produced from the red substance $C_{28}H_{14}O_6$ by the simple addition of oxygen, thus:—

$$C_{28}H_{14}O_6 + O = C_{28}H_{14}O_7.$$

Crystallised from a mixture of aniline or nitrobenzene and alcohol, this substance $C_{28}H_{14}O_7$ appears under the microscope as groups of short, colourless needles. From hot acetone, however, in which it is only very slightly soluble, it can be obtained in larger crystals. It is slightly soluble in coal-tar naphtha, more soluble in acetic acid. When heated, it melts at a high temperature to a yellow liquid, which on cooling solidifies to a hard, crystalline mass. At higher temperatures it chars, only a very small quantity subliming in microscopic needles. $C_{28}H_{14}O_7$ dissolves readily in hot aniline or nitrobenzene, and the solutions on cooling deposit small plates of a brownish colour. These substances, which are evidently additive compounds of $C_{28}H_{14}O_7$ with aniline and nitrobenzene, have not as yet been analysed. They are readily obtained pure by adding cautiously to the hot solution in aniline or nitrobenzene about twice the volume of benzene. On cooling, the compound separates out in glistening plates. On boiling with alcohol, they are quickly split up into their constituents.

Boiled with zinc-dust and potash solution, $C_{28}H_{14}O_7$ slowly dissolves, forming a reddish-brown solution, which on shaking with air instantaneously decolorises with precipitation of a white, gelatinous substance.

The following reaction is characteristic of this substance:—If a trace be boiled with a strong solution of potash in methyl alcohol in a test-tube, it will gradually dissolve, with an olive-green coloration. On continued boiling, the solution becomes darker and darker coloured as the methyl alcohol evaporates, the green gradually changing to a beautiful brownish-pink. On adding water, a violet solution is obtained, which does not decolorise on shaking with air, and therefore possibly consists of potassic alizarate.

Action of Nitric and Sulphuric Acids on $C_{28}H_{14}O_6$.

If $C_{28}H_{14}O_6$ is treated with a mixture of nitric and sulphuric acids, a reaction quite different from the above takes place. In studying this, a small quantity of substance was boiled with a mixture of equal parts of nitric and sulphuric acids for a short time, the product poured into water, and the precipitate well washed and dried. In order to purify it, it was dissolved in hot acetic anhydride, the solution poured into an equal bulk of hot alcohol, and allowed to cool slowly. A beautiful yellow, crystalline powder was thus obtained, which on heating with potassium and then testing with ferrous and ferric chlorides, was found to contain a considerable amount of nitrogen. We have not as yet analysed this nitro-derivative, but its properties resemble very much those of the nitroanthraquinones except that it does not sublime when heated, but is almost entirely decomposed, leaving a black residue. If heated with sulphuric acid, a violent reaction sets in, and on diluting the product with water, a red-violet precipitate is obtained, which dissolves in potash with a blue colour. When boiled with sodium sulphide, a brick-red amido-compound is obtained, resembling amidoanthraquinone, with which, however, it does not appear to be identical.

Fusion of $C_{28}H_{14}O_7$ *with Potash.*

In carrying out this experiment, the substance was heated in a closed iron tube with concentrated potash solution for 12 hours at 180°. The product was then boiled with water, filtered, a small quantity of lime added to the violet-blue filtrate, again filtered, and the residual violet powder washed with water and decomposed with hydrochloric acid.

The orange-coloured precipitate formed was washed with water, dried, and once or twice recrystallised from benzene. Red needles were thus obtained which melted at about 285°, and showed all the properties of alizarin. The analysis gave the following numbers:—

0·1471 gram substance gave 0·0488 gram H_2O and 0·3749 gram CO_2.

	Theory. $C_{14}H_8O_4$.	Found.
C.....	70·00 per cent.	69·57 per cent.
H	3·33 „	3·62 „
O.....	26·66 „	26·81 „

The filtrate from the alizarate of lime was a red solution with a green fluorescence, which on acidifying gave a white precipitate, changing to green on washing. This substance, of which only a minute quantity was obtained, appeared to be unattacked $C_{28}H_{14}O_7$.

That portion of the product which was insoluble in water, after repeated recrystallisation from glacial acetic acid, appeared under the microscope as orange-red needles, giving with sulphuric acid a reddish-violet solution, and in all other respects showing the properties of the red substance $C_{28}H_{14}O_6$. Dried at 120°, it gave the following results on analysis:—

0·0859 gram substance gave 0·0269 gram H_2O and 0·2365 gram CO_2.

	Theory. $C_{28}H_{14}O_6$.	Found.
C.....	75·34 per cent.	75·09 per cent.
H	3·14 „	3·48 „
O.....	21·52 „	21·43 „

Two distinct reactions therefore take place when $C_{28}H_{14}O_7$ is fused with potash.

In the first place the elements of water are taken up, 1 mol. of $C_{28}H_{14}O_7$ splitting up into 2 mols. of alizarin, thus:—

$$C_{28}H_{14}O_7 + H_2O = 2C_{14}H_8O_4,$$

whereas at the same time a certain amount of reduction takes place, some of the $C_{28}H_{14}O_7$ being reduced to the original red substance, thus:—

$$C_{28}H_{14}O_7 + H_2 = C_{28}H_{14}O_6 + H_2O.$$

Action of Chromic Acid on $C_{28}H_{14}O_7$.

In the first paper on these anthraquinone-derivatives (*loc. cit.*, p. 683), we showed that when the red substance $C_{28}H_{14}O_6$ is oxidised with chromic acid in acetic solution it is converted into a white substance of the formula $C_{14}H_8O_4$, thus:—

$$C_{28}H_{14}O_6 + O_2 = 2C_{14}H_8O_4 + H_2O.$$

On considering the results just described, it appeared likely that the substance $C_{28}H_{14}O_7$ was really the first product of the action of oxidising agents on $C_{28}H_{14}O_6$, and that this, therefore, on further oxidation should yield the same substance, $C_{14}H_6O_4$, as is obtained direct by the action of chromic acid on $C_{28}H_{14}O_6$. In order to decide this point, a small quantity of the substance $C_{28}H_{14}O_7$ was dissolved in hot glacial acetic acid, and treated with chromic acid until the violent reaction which set in at first had subsided. On allowing the green solution to cool, a white, crystalline powder was deposited. This was collected, washed, dried, and several times recrystallised from glacial acetic acid.

In this way the product was easily separated into two portions, one of which was considerably more soluble in acetic acid than the other.

The less soluble portion on analysis gave the following numbers:—

0·1583 gram substance gave 0·0385 gram H_2O and 0·4100 gram CO_2.

	Theory. $C_{14}H_6O_4$.	Found.
C.....	70·59 per cent.	70·63 per cent.
H	2·52 „	2·70 „
O.....	26·89 „	26·67 „

The substance therefore has the formula $C_{14}H_6O_4$, and a careful comparison showed that it is without doubt identical with that produced by the direct oxidation of the red substance $C_{28}H_{14}O_6$ with chromic acid. Attempts to produce the substance $C_{28}H_{14}O_7$ by cautious oxidation of $C_{28}H_{14}O_6$ with chromic acid were unsuccessful, the reaction in all cases going as far as the formation of the compound $C_{14}H_6O_4$.

The more soluble substance obtained in the above oxidation was found on examination to consist of unchanged substance, as the following analysis shows:—

0·1699 gram substance gave 0·0490 gram H_2O and 0·4520 gram CO_2.

	Theory. $C_{28}H_{14}O_7$.	Found.
C.....	72·72 per cent.	72·51 per cent.
H	3·03 „	3·20 „
O.....	24·25 „	24·29 „

Action of Hydriodic Acid on $C_{28}H_{14}O_6$.

Experiments were next made with the object of removing some of the oxygen-atoms from the molecule $C_{28}H_{14}O_6$ in the hope of thus

obtaining some well-known compound, the formation of which might throw additional light on the nature of the red substance.

If $C_{28}H_{14}O_6$ is suspended in hot glacial acetic acid, and fuming aqueous hydriodic acid added drop by drop, the crystals rapidly dissolve, forming a deep red solution which contains free iodine; this is filtered and poured into water, when a lemon-yellow precipitate is deposited, which is collected, well washed, dried, and purified by recrystallisation from a mixture of hot aniline and alcohol; on cooling, it is deposited as a yellow, crystalline powder. Two different samples dried at 110° were analysed with the following results:—

I. 0·1457 gram substance gave 0·0470 gram H_2O and 0·4160 gram CO_2.

II. 0·0659 gram substance gave 0·0212 gram H_2O and 0·1880 gram CO_2.

	Found.		Theory.	
	I.	II.	$C_{28}H_{14}O_5$.	$C_{28}H_{16}O_5$.
C.....	77·86	77·80 p. c.	78·14	77·77 p. c.
H.....	3·58	3·57 „	3·26	3·70 „
O.....	18·56	18·53 „	18·60	18·52 „

The numbers obtained agree, therefore, better with the formula $C_{28}H_{14}O_5$ than with $C_{28}H_{16}O_5$, and it is probable that this new compound is formed from the red substance simply by elimination of oxygen, thus:—

$$C_{28}H_{14}O_6 + H_2 = C_{28}H_{14}O_5 + H_2O.$$

This substance, $C_{28}H_{14}O_5$, which is insoluble in aqueous potash, dissolves in a strong, hot solution of potash in methyl alcohol, with an intense orange-brown colour which on long boiling does not change. If the alcohol is evaporated, the colour becomes intenser as the solution becomes stronger, until at last a dark-brown residue is left; this dissolves in water with an orange-red colour, which, however, almost disappears on shaking with air.

When boiled with zinc-dust and potash, $C_{28}H_{14}O_5$ gives scarcely any coloration, but it dissolves in concentrated sulphuric acid, forming an intense reddish-brown solution.

The ease with which the red substance $C_{28}H_{14}O_6$ loses 1 atom of oxygen, and is reduced to $C_{28}H_{14}O_5$, led us to think that it would be interesting to study the further action of hydriodic acid on this substance. For this purpose, a mixture of 0·5 gram of the pure red substance, 5 grams of fuming hydriodic acid, and 5 grams of glacial acetic acid were heated in a sealed tube for about half an hour to 160°. The dark-red liquid thus obtained was gently evaporated to get rid of most of the acetic acid, the residue freed from iodine by

boiling with dilute aqueous sulphurous acid. The precipitate, which separated on cooling, was collected, filtered, washed with water, and dried on a porous plate. On extracting the product with alcohol, nearly the whole dissolved, leaving a small quantity of a yellow substance behind. This residue, after careful drying and sublimation in a test-tube, formed microscopic yellow needles melting at about 260—265°, and which on boiling with potash solution and zinc-dust gave a red solution becoming colourless again on shaking with air. This substance was, therefore, probably anthraquinone.

The alcoholic solution on evaporation deposited a considerable quantity of a somewhat sticky yellow substance, which, especially when boiled with water, possessed in a marked degree the peculiar odour of dihydroanthracene. In order to determine whether the reduction really had gone as far as this, the crude substance was distilled in a test-tube, the solid distillate washed with a little alcohol, and then recrystallised from this solvent. In this way, small crystals were obtained which melted at 104—106°, and otherwise showed all the properties of dihydroanthracene.

Action of Sulphuric Acid on $C_{28}H_{14}O_7$.

In studying this action, a small quantity of the substance was heated with fuming sulphuric acid at 180°. The reddish-brown solution first formed became gradually darker and eventually, after 20 minutes' heating, of a bluish-red colour. At this stage, the decomposition was evidently complete, the product dissolving completely in water, showing that a sulphonic acid had been formed. On adding acetic acid to the strong hot solution, and allowing it to cool, a small quantity of a crystalline precipitate separated. It was, however, found impracticable to purify the sulphonic acid by this method, as it was too soluble in acetic acid to admit of sufficient washing. The mixture of the sulphonic acid and sulphuric acid dissolved in water forming a greenish solution, with which lead or barium carbonate yielded insoluble compounds only.

In order, if possible, to determine the nature of the sulphonic acid thus formed, resort was had to fusion with potash. The solution was mixed with a considerable excess of concentrated aqueous potash, and heated in closed iron tubes at 180° for about 12 hours. The product dissolved in water, forming a red-violet solution, and on the addition of acids a brownish-yellow precipitate was thrown down, which was collected and well washed with water. This substance dyed mordanted cloth shades intermediate between those given by anthrapurpurin and flavopurpurin, and, therefore, probably consists of a mixture of these two substances.

Fusion of $C_{14}H_8O_4$ *with Potash.*

This substance, the preparation of which was given in the previous paper (*loc. cit.*, p. 683), is formed by the oxidation of the red substance, $C_{28}H_{14}O_6$, with chromic acid in acetic acid solution. Considering the interesting constitution previously assigned to this substance and its mode of formation from the red substance, it was thought that valuable results might be obtained from the further study of its properties. The first decomposition which was studied was the action of caustic potash at high temperatures on this substance. Two grams of pure $C_{14}H_6O_7$ were heated with concentrated potash solution for about 12 hours at 180°, the dark-coloured product extracted with boiling water and filtered. A small quantity of lime was then added to the bluish-violet filtrate, the lime compound thus precipitated, collected, washed with water, and decomposed with dilute hydrochloric acid. This caused the precipitation of an orange-red compound, which after collecting, washing with water, drying and recrystallising once or twice from benzene, was obtained in long red needles; it melts at about 285°, and possesses all the properties of alizarin.

The analysis gave the following numbers:—

0·1175 gram substance gave 0·0391 gram H_2O and 0·1175 gram CO_2.

	Theory. $C_{14}H_8O_4$.	Found.
C.....	70·00 per cent.	69·98 per cent.
H.....	3·33 „	3·69 „
O.....	20·67 „	20·43 „

The portion of the product insoluble in water obtained during the fusion of $C_{14}H_6O_2$ with potash, was extracted several times with glacial acetic acid, and boiling water added to the filtrate. On cooling, long orange-coloured needles were deposited which on analysis gave numbers corresponding with the formula $C_{14}H_8O_2$.

I. 0·1235 gram substance gave 0·0463 gram H_2O and 0·3648 gram CO_2.

II. 0·1285 gram substance gave 0·0466 gram H_2O and 0·3800 gram CO_2.

	Theory. $C_{14}H_8O_2$.	Found.	
		I.	II.
C	80·77 p. c.	80·60	80·65 p. c.
H.....	3·84 „	4·17	4·03 „
O	15·39 „	15·23	15·32 „

This compound, obtained by the fusion of $C_{14}H_8O_4$ with potash, did not at all resemble anthraquinone outwardly, as, however often it was

recrystallised, it was always deposited in flat, silky needles of an orange colour. It melted, however, at 275°, the melting point of anthraquinone, and when heated strongly it sublimed much in the same way as ordinary anthraquinone, so that there can be no doubt as to its identity with that substance.

The action of caustic potash on $C_{14}H_6O_4$ appears, therefore, to be entirely a reducing action, alizarin and anthraquinone being formed according to the equations—

$$\text{I. } C_{14}H_6O_4 + H_2 = C_{14}H_8O_4,$$
$$\text{II. } C_{14}H_6O_4 + 3H_2 = C_{14}H_8O_2 + 2H_2O.$$

Action of Sulphuric Acid on $C_{14}H_6O_4$.

In studying this reaction, the substance $C_{14}H_6O_4$ was heated with three or four parts of Nordhansen sulphuric acid at 200° until a sample taken out dissolved entirely in water. As soon as this was found to be the case, the product was poured into glacial acetic acid drop by drop, the whole being constantly stirred during the operation. This caused the separation of a white substance which, when examined under the microscope, was seen to consist of a mass of small crystals. When the precipitation was complete, about twice the bulk of glacial acetic acid was added, the mixture thrown on a filter, washed with glacial acetic acid till free from sulphuric acid, and then well drained. The product was dissolved in a little water, and alcoholic soda added to the solution until the white crystalline salt thus formed had been completely precipitated. After collecting, well washing with alcohol and drying at 100°, this salt gave the following numbers on analysis :—

0·1963 gram substance gave 0·0333 gram H_2O.
0·3540 gram CO_2.
0·0415 gram Na_2SO_4.

	Theory. $C_{14}H_5O_4.SO_3Na$.		Found.	
C.....	49·41	per cent.	49·18	per cent.
H	1·47	„	1·88	„
Na	6·76	„	6·84	„
O.....	32·95	„	—	
S.....	9·41	„	—	

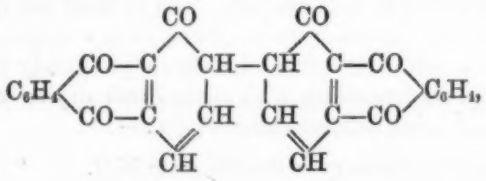
Solutions of this salt give precipitates with salts of copper, lead, barium, and other metals. On fusion with potash, this sulphonic acid yields a reddish-violet solution which, on addition of acids, deposits a yellow precipitate. This after being collected and washed

with water, was found to dye mordanted cloths shades very closely resembling those produced by flavopurpurin. As the substance also gave the same absorption-bands as flavopurpurin there can be no doubt of its identity with this substance.

In order to examine more completely the action of sulphuric acid on $C_{14}H_6O_4$, the acetic acid filtrate from the precipitated sulphonic acid was next experimented on, thus:—After distilling off the acetic acid, the residue was dissolved in potash, fused with an excess of strong potash solution in an iron tube, and the product isolated in the usual way. The yellowish-brown flocculent precipitate thus obtained dyed mordanted cloth with shades slightly yellower than, but otherwise exactly similar to, those produced by anthrapurpurin, and a careful examination of the substance showed that it agreed with this compound in all its reactions. By the action of Nordhausen sulphuric acid on $C_{14}H_6O_4$, it would appear, therefore, that two sulphonic acids are formed, of which one is insoluble and the other soluble in glacial acetic acid. On fusion with potash, the former yields flavopurpurin and the latter anthrapurpurin.

Theoretical Remarks.

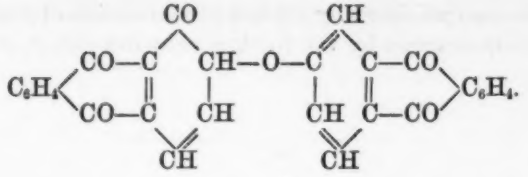
On considering the results described in the body of this paper, it appears very doubtful whether the red substance $C_{28}H_{14}O_6$ can have the formula first assigned to it (*loc. cit.*, p. 684), namely—



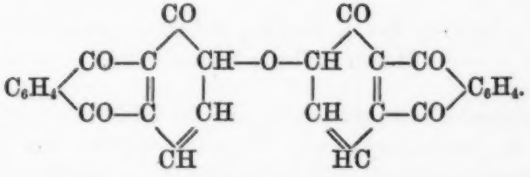
as this formula does not in any way explain the formation of the oxidation compound $C_{28}H_{14}O_7$, or the decomposition into alizarin by fusion with potash. A reaction of this kind would involve the severing of the two anthraquinone molecules, which would hardly take place so easily if they were joined simply carbon to carbon, as shown above.

In order to be able to explain the formation of its various derivatives, it is necessary to suppose that the two anthraquinone molecules are linked together in a much more feeble way, as for instance with the intervention of an oxygen-atom.

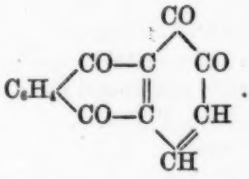
The most probable formula for the red substance $C_{28}H_{14}O_6$, and one which would explain all its decompositions, would be—



By the action of nitric acid this substance is converted into $C_{28}H_{14}O_7$, which would be represented by the formula—



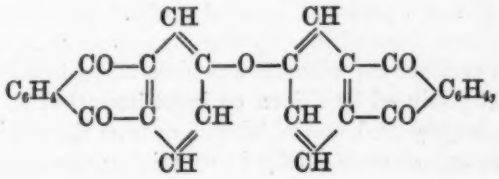
On further oxidation this substance is converted into 2 mols. of $C_{14}H_6O_4$, a change which is easily understood if we assume that the latter substance has the constitution which was previously assigned to it; that is—



There is every reason to believe that this substance has the simple formula $C_{14}H_6O_4$, and not the double formula $C_{28}H_{12}O_8$. The comparatively low melting point of this substance (about 300°), and the fact that it sublimes easily and completely when heated, almost exclude the possibility of its having the double molecular weight $C_{28}H_{12}O_8$.

The constitutional formula given above for this substance easily explains the reduction to alizarin and anthraquinone by the action of potash at a high temperature.

Lastly, the substance $C_{28}H_{14}O_5$, produced by the action of hydriodic acid on $C_{28}H_{14}O_6$, would be represented by the formula—



which in its turn would easily explain the formation of anthraquinone and dihydroanthracene by the further reducing action of hydriodic acid.

LXX.—*The Influence of Silicon on the Properties of Iron and Steel.* Part II.

By Thomas Turner, Assoc. R.S.M., F.I.C., Lecturer on Metallurgy, Mason College, Birmingham.

In the first part of this paper (Trans., 1887, **51**, 129), a brief *résumé* was given of previous experiments on this subject, and observations were described connected with the influence of silicon on the purest form of iron which can be obtained commercially in considerable quantities, and in the fluid condition, viz., the metal produced in the basic process, at the end of the blow, and before any addition of carbon or manganese has been made. From this material, ingots were prepared, containing gradually increasing proportions of silicon, and by combined chemical and mechanical testing the following conclusions were arrived at. The metal being, as above stated, very low in manganese, was originally rather red short, and this red shortness was increased by the presence of silicon, so much so that all ingots containing over 0·13 per cent. of silicon crumbled to pieces in the rolls. Silicon increased the tensile strength and limit of elasticity; it also rendered the metal quiet in the mould; the elongation and contraction of area were both considerably diminished, however, and the fracture changed in character from finely silky to crystalline. On the other hand, silicon had no apparent influence on the welding property of the iron. At the same time it was pointed out that these results were only true under the circumstances of the experiments, and that in the presence of larger quantities of other elements the influence of silicon would doubtless be considerably modified. The results of the above experiments differ in one or two important particulars from what is observed commercially with ingot iron containing about half a per cent. of manganese, which is one of the purest forms of metal produced by steel works. The results differ in the same way from those of the experiments now to be described.

The present series of experiments was undertaken in order to determine the effect produced by silicon on ingot iron, that is, the "mild steel" now so largely used, and which differs from the metal employed in the previous experiments chiefly in containing about one-tenth per

cent. more carbon, and a half per cent. more manganese. The experiments were conducted as before at the works of the South Staffordshire Steel and Ingot Iron Company, Bilston, and the general method of procedure was very similar to that described in Part I, though a few alterations in detail were necessary. A weighed quantity of the same siliceous iron (10·3 per cent. silicon) as had been previously used was placed in a covered clay crucible, which was heated in a small reverberatory furnace to the melting point of cast iron; at the same time a second and exactly similar crucible was heated in the same way, and to the same temperature. The crucibles were capable of holding about 40 lbs. of metal. At the conclusion of the blow, after the addition of ferromanganese had been made, and the metal teemed into the ladle, the crucibles were rapidly brought from the furnace, and the one containing the siliceous iron was filled up with ingot iron, from about the middle of the cast. After standing for about a minute, and while the contents of the crucible were still thoroughly fluid, the metal was poured into the other red-hot crucible, so as to ensure as nearly as possible perfect mixture. In the second crucible the metal was allowed to solidify, and the ingots so obtained were examined as in the previous experiments. I have again gratefully to acknowledge the important assistance received in conducting these experiments. The rolling of the specimens and the works tests were superintended by Mr. F. W. Harbord, of Bilston; the mechanical testing was performed by Professor A. B. W. Kennedy, with the University College testing machine; whilst the whole of the chemical analyses were conducted by Mr. J. P. Walton, of Wishaw. The author's part has been merely the preparation of the ingots, and the general arrangement of the experiments and of the results.

Works Tests. (See Table A.)

The ingots were reheated and rolled by workmen accustomed to the manipulation of mild steel; no special care was given so as to humour the metal, the desire being to give all the ingots as fair a test as possible. In each case the ingots rolled satisfactorily, and the required round bar of $1\frac{1}{8}$ inch diameter was obtained. In each case also the hot test was satisfactory. These results are quite different from what was noticed when manganese was absent, but they accord with observations of experienced steel makers. It may be mentioned that the hot test employed was that commonly used at the works, the bar being plated out hot, doubled flat upon itself across the middle of the plated portion, and the doubled part bent again at right angles to the first bend. In the cold, or bending test, all the samples behaved well, with the single exception of No. 11, which contained not only 0·504 per

TABLE A.—*Influence of Silicon on Ingot Iron. General Summary of Results.*

No.	Chemical Analyses. (By J. P. Walton.)					Works Tests. (By F. W. Harbord.)				Mean of Mechanical Tests. (By Professor A. B. W. Kennedy.)						Relative hardness.
	Si.	C.	S.	P.	Mn.	Rolling.	Hot.	Cold.	Welding.	Limit of elasticity.	Breaking load.	Ratio of limit to break.	Extension per cent. on 10 inches.	Reduction of area per cent.	Work done per cubic inch.	
										tons.	tons.				tons.	
1	0·010	0·16	0·050	0·060	0·550	Rolled well.	Good.	Perfect.	Perfect.	22·00	29·64	0·743	23·1	48·8	6·25	Differences so small as to be scarcely perceptible.
2	0·061	0·16	0·028	0·058	0·619	„ „	„	„	„	22·21	31·61	0·703	20·4	40·7	5·80	
3	0·070	0·15	0·084	0·051	0·500	„ „	„	Good.	„	21·05	29·51	0·713	22·9	51·5	6·12	
4	0·092	0·21	0·084	0·064	0·634	„ „	„	Perfect.	„	22·43	33·66	0·666	19·4	44·1	5·82	
5	0·102	0·18	0·028	0·066	0·662	„ „	„	Good.	„	21·26	33·57	0·634	20·6	51·4	6·06	
6	0·121	0·19	0·064	0·068	0·576	„ „	Good, but rather red-short at welding heat.	„	„	22·70	31·86	0·712	21·9	43·7	6·31	
7	0·135	0·13	0·028	0·057	0·480	„ „	Good.	„	„	21·29	29·42	0·724	24·8	56·6	6·62	
8	0·247	0·19	0·028	0·074	0·642	„ „	„	„	„	22·23	34·70	0·640	17·6	49·6	5·36	
9	0·320	0·15	0·040	0·081	0·490	„ „	„	„	„	22·32	33·23	0·671	16·7	36·1	4·96	
10	0·382	0·16	0·042	0·087	0·533	„ „	„	Perfect.	„	24·72	35·67	0·693	18·0	30·7	5·79	
11	0·504	0·18	0·094	0·121	0·455	„ „	„	Broke short off at 50°.	„	26·35	36·72	0·717	19·4	34·8	6·45	

cent. of silicon, but also 0·121 of phosphorus. It is not at all certain that the sample would have proved quite so brittle in the absence of phosphorus. It is to be regretted that the comparatively small scale on which the experiments were performed precluded accurate tests as to resistance to shock, but so far as these experiments have gone they appear to show that there is certainly no appreciable brittleness in ingot iron until the proportion of silicon reaches 0·25 per cent. Beyond that proportion the character of the other tests would lead us to expect more or less brittleness. The welding tests, as in the previous experiments, were all perfect, and silicon appears to be without influence in this respect. (Compare Trans., 1887, **51**, 141.)

Chemical Composition.—An examination of the results of chemical analysis (given in Table A) shows that the silicon gradually increases throughout the series. It should be explained that Sample No. 1, which is given for comparison, represents ingot iron to which no silicon has been added. The composition shown is about what may be expected in good quality ingot iron of this kind, whilst the mechanical values are derived from four separate tests made by Professor Kennedy on metal which had been produced, on two separate occasions, by treating ingot iron in precisely the same way as in the other cases when silicon was added. In experiments of this kind it is of course extremely difficult to keep all the other constituents quite constant while silicon varies, and in the deductions which are drawn from these experiments I have endeavoured, as far as possible, to make allowance for the known effect of the variations observed before drawing any conclusion as to the influence of silicon. The *maximum* variations observed are as follows:—Carbon, 0·08 per cent.; sulphur, 0·056 per cent.; phosphorus, 0·036 per cent. (in a single instance previously mentioned this is exceeded); and manganese, 0·207 per cent.

Mechanical Tests.—These were performed in duplicate, the actual results being given in Table B; the mean values deduced from these experimental data being given in Table A. It will be seen from Table A that the two experiments with each sample generally gave values which agreed very fairly well with each other. The greatest variations are noticed in the elongation and contraction of area where, in a few cases, very considerable differences are noticed. Some allowance must, of course, be made on account of the small scale on which the experiments were conducted; but it may be pointed out that in the previous series of experiments, as in the present case, the samples low in silicon are distinctly more regular than those containing a larger proportion of this element; hence the results support the views of M. Pourcel, that silicon renders the contraction of area and the elongation irregular.

TABLE B.—*Mechanical Tests. Professor A. B. W. Kennedy's Results.*

No.	University College No.	Silicon per cent.	Limit of elasticity per sq. inch.		Breaking load per square inch.		Ratio of limit to break.	Extension per cent. on 10 inches.	Reduction of area at fracture per cent.	Work done in fracture per cubic inch. In. tons.	Fracture.
			Pounds.	Tons.	Pounds.	Tons.					
1	Original metal, mean of 4	0·01	49,280	22·00	66,385	29·64	0·743	23·1	48·8	6·25	Silky, with a few small crystalline spots.
2	12,296	0·061	49,400	22·06	70,040	31·26	0·706	23·0	48·4	6·48	Silky, a few finely crystalline spots.
	12,297		50,100	22·37	71,580	31·96	0·700	17·8	33·1	5·12	Silky, one small finely crystalline patch.
3	12,284	0·07	45,480	20·31	65,900	29·43	0·690	22·1	49·3	5·83	Silky, with several small crystalline spots.
	12,285		48,800	21·79	66,270	29·59	0·736	23·8	53·7	6·42	Finely crystalline, with one granular patch.
4	12,280	0·092	48,860	21·82	74,760	33·38	0·654	20·1	42·2	5·94	Silky, with about a dozen crystalline spots.
	12,281		51,600	23·04	76,000	33·94	0·679	18·8	46·1	5·70	Silky, finely granular in centre; a few crystalline spots.
5	12,292	0·102	45,550	20·33	74,020	33·04	0·615	22·7	52·0	6·54	Silky, a few finely crystalline spots.
	12,293		49,750	22·21	76,160	34·01	0·653	18·6	50·9	5·59	Silky, two crystalline spots about $\frac{1}{16}$ inch diameter.
6	12,278	0·121	51,570	23·02	71,640	31·98	0·720	21·2	42·7	6·15	Silky, irregular; several crystalline spots, one about $\frac{1}{16}$ inch diameter.
	12,279		50,100	22·37	71,100	31·75	0·705	22·6	44·8	6·47	Edge silky; about 90 per cent. finely crystalline, with a dozen spots.
7	12,288	0·135	47,330	21·13	67,120	29·96	0·705	24·3	57·2	6·56	Silky, a few specks crystalline.
	12,289		48,060	21·46	64,680	28·88	0·743	25·3	56·0	6·68	Silky, some spots of hard crystal.
8	12,294	0·247	46,490	20·75	75,780	33·83	0·613	20·3	48·4	5·98	Silky, a few finely crystalline spots.
	12,295		53,110	23·71	79,700	35·58	0·666	15·0	50·9	4·74	Do. do.
9	12,290	0·320	51,280	22·89	75,470	33·70	0·679	17·0	28·8	5·12	Silky; a spot of hard crystal $\frac{1}{8}$ inch diameter, fissured and unsound in centre.
	12,291		48,720	21·75	73,380	32·76	0·664	16·5	43·8	4·80	Silky, but fissured and unsound throughout.
10	12,282	0·382	54,300	24·25	79,800	35·63	0·681	12·7	10·7	4·04	Crystalline throughout.
	12,283		56,420	25·19	80,000	35·72	0·705	23·4	50·8	7·54	Finely crystalline granular; silky at edges.
11	12,286	0·504	59,120	26·40	81,300	36·30	0·727	18·5	34·0	6·10	Finely crystalline, with one granular patch.
	12,287		58,930	26·31	83,180	37·14	0·708	20·3	35·6	6·81	Finely but irregularly crystalline; narrow rim at edge, silky.

Limit of Elasticity.—This is rather high (22 tons) in the original metal, and in the mean results (Table A) varies over a maximum range of 1·65 tons in the six following samples (Nos. 2 to 7). These small differences are precisely of the kind which can be accounted for by the observed variations in the other constituents present, and the addition of 0·135 per cent. of silicon does not appear to have produced any important alteration in the limit of elasticity. The limit is, however, distinctly raised with more silicon.

Breaking Load.—This varies in a manner almost exactly like that of the elastic limit. It is high in the original metal (29·64 tons), and in the six following samples shows a maximum range of 4·1 tons, due apparently to circumstances other than the proportion of silicon. With more silicon, however, the breaking load is distinctly raised.

Extension.—The extension is rather below the average for such metal in the original sample and in the first six specimens, but is about what would be anticipated from the other mechanical properties of the metal. The average of the values for the extension of these six samples is rather lower than that of the original metal, so that the influence of silicon, though slight, is probably not beneficial. The irregular and lower results are more marked with larger proportions of silicon.

Reduction of Area.—This, as would be expected, follows closely in the order of extension, and is distinctly low and irregular with the larger percentages of silicon.

Appearance of Fracture.—In the first specimen, the fracture is almost entirely silky in appearance, the intermediate specimens show greater tendency to granular or crystalline structure, while the specimens with most silicon were most crystalline or granular, and the fracture in several instances showed considerable irregularity. These results tend to show that the influence of several tenths per cent. of silicon is not beneficial.

Conclusions.

Ingot iron containing silicon in all proportions up to 0·5 per cent. (and with about 0·5 per cent. of manganese) rolls well, and does not show any signs of red shortness; it welds perfectly with all proportions of silicon, and, with the somewhat doubtful exception of the 0·5 per cent. specimen, is not brittle when cold. With less than about 0·15 per cent. of silicon, the limit of elasticity, the breaking load, the extension, and the reduction of area, are but little, if at all, affected by the proportion of silicon present. The fracture, though not much altered, shows rather greater tendency to a crystalline or granular appearance. With upwards of 0·15 per cent. of silicon the

limit of elasticity and breaking load are increased, though the effect of silicon in this respect is not nearly so marked as that of carbon. The reduction of area and extension (that is the ductility) are distinctly reduced, and rendered more irregular by the presence of much silicon. The fracture is also rendered more granular or crystalline, and is less regular in character.

LXXI.—*The Isonitrile of Phenylhydrazine.*

By S. Ruhemann, Ph.D., and W. J. Elliott.

Isonitriles derived from hydrazines have not been carefully examined, and as such an investigation seemed desirable, we undertook their examination, and now communicate to the Society the results of our experiments on the isonitrile of phenylhydrazine.

For the preparation of this isonitrile, phenylhydrazine is dissolved in alcoholic potash and chloroform is carefully added to the solution. After heating in a water-bath for half an hour, the flask is cooled, the product diluted with water and shaken with ether. The unaltered phenylhydrazine is removed from the ethereal solution of the isonitrile by shaking with very dilute sulphuric acid. On evaporating the ethereal solution, a brown oil remains, which has a penetrating odour of isonitrile and partially solidifies on cooling. The crystalline mass thus obtained is dissolved in alcohol, from which spherical aggregations of pale-yellow needles, devoid of odour, separate. The alcoholic filtrate almost entirely loses the odour of isonitrile on standing for a few days, and on evaporating the greater part of the alcohol, deposits a small quantity of the same crystals, while the filtrate from these contains an uncrystallisable resin.

The crystals thus obtained become quite white on recrystallising several times from alcohol. The pure substance melts at 180°, is easily soluble in chloroform, carbon bisulphide, and acetic acid, as well as in alcohol and in ether, but is insoluble in water and is not volatile in steam.

The results of analysis indicate the empirical formula $C_7H_6N_2$:—

	Calculated for $C_7H_6N_2$.	Found. I.	Found. II.
C	71·19	71·08	—
H	5·08	5·46	—
N	23·73	—	23·82
	100·00		

Hence this substance has the percentage composition required for the isonitrile of phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NC$; but it is shown not to have this composition by the absence of the characteristic odour of the isonitriles and by its chemical behaviour. It is very probable that the crystals which melt at 180° are the result of a change which the initially formed isonitrile undergoes; for in some preparations crystals did not separate out from the oil immediately after evaporation of the ether, but only on standing for some time.

It is possible that the stable compound consisted of the normal cyanide $C_6H_5{\cdot}NH{\cdot}CN$, and in that case we should have had the molecular transformation of an isonitrile into a normal nitrile taking place at a lower temperature than the corresponding change of the isonitriles of aniline and its homologues. In order to determine whether the substance obtained from phenylhydrazine was the normal nitrile, its behaviour with acids and particularly with hydrochloric acid was studied.

The compound when heated at 200° with hydrochloric acid in a sealed tube is only slightly altered. The tube contains bluish crystals which are soluble in alcohol, leaving behind a small quantity of a blue residue with metallic lustre. White needles are deposited from the alcoholic solution, which were proved to be the original compound by their melting point and by a nitrogen determination, which gave 23·94 per cent. of N. The substance undergoes no change on heating at 100° with alcoholic potash.

Hofmann (*Ber.*, **17**, 1914; **18**, 1825) failed to convert the cyanides of tetra- and penta-methylaniline into the corresponding acids. Hence the stability of this compound towards hydrochloric acid does not conclusively prove that it is not a cyanide. Further investigation, however, showed that we are here dealing with the representative of another class of substances.

We next proceeded to find the molecular weight of the compound. This cannot be done by a vapour-density determination, because partial decomposition takes place at the high temperature required for vaporisation. In consequence we employed Raoult's method of determining molecular weights, and used for the purpose the simple apparatus described by Holleman (*Ber.*, **21**, 860), which gave very satisfactory results.

The solvent used was glacial acetic acid, the freezing point of which was 14·39°. 0·2931 gram of the substance dissolved in 18·9784 grams of acetic acid depressed the freezing point by 0·25°, which corresponds to the molecular weight 240.

It follows from this determination that the empirical formula derived from direct analysis should be doubled. The formula $C_{14}H_{12}N_4$ thus obtained requires a molecular weight of 236. Further

confirmation of this formula is furnished by the behaviour of the substance with nitric and sulphuric acids.

When a solution of the compound in glacial acetic acid is treated with fuming nitric acid, a lemon-yellow crystalline precipitate forms at once. This is insoluble in water but soluble in boiling glacial acetic acid, from which it separates on cooling in microscopic needles which melt at a temperature lying above 300°.

A nitrogen determination shows the compound to have the formula $C_{14}H_{11}N_4 \cdot NO_2$.

	Calculated for $C_{14}H_{11}N_4 \cdot NO_2$.	Found.
N	25·10	24·91

When the substance formed from phenylhydrazine is heated with concentrated sulphuric acid it dissolves; if the heating is continued till no precipitate is formed immediately on the addition of water to a drop of the solution, and the cold solution is then poured into water, tufts of white needles crystallise out on long standing. These crystals, which contain sulphur, are insoluble in alcohol, benzene, and chloroform, only sparingly soluble in cold water. After crystallisation from hot water they give on analysis numbers which correspond to the formula $C_{14}H_{11}N_4 \cdot HSO_3$.

	Calculated for $C_{14}H_{11}N_4 \cdot HSO_3$.	Found. I.	Found. II.
N	17·36	17·72	—
S	10·20	—	10·126

This substance, therefore, is a sulphonic acid. It forms an ammonium salt and a barium salt not easily soluble in water.

The molecular weight as determined by Raoult's method, together with the formation of the nitro-compound $C_{14}H_{11}N_4 \cdot NO_2$, and the sulphonic acid $C_{14}H_{11}N_4 \cdot HSO_3$, prove that the compound obtained from phenylhydrazine in the manner described above has the formula $C_{14}H_{12}N_4$.

When we consider the mode of formation and the chemical behaviour of the compound $C_{14}H_{12}N_4$, there can be scarcely any doubt that its constitution is expressed by the formula—

$$C_6H_5 \cdot NH \cdot N : C : C : N \cdot NH \cdot C_6H_5.$$

The pentad nitrogen of the isonitrile passes into the triad condition by the union of two molecules of the isonitrile $C_6H_5 \cdot NH \cdot NC$; whereas in all aromatic isonitriles known up to the present time, the corresponding change takes place by the molecular transformation of the isonitrile into the normal nitrile.

Further experiments with secondary as well as primary hydrazines are in progress, in order to determine whether they show the same behaviour as phenylhydrazine.

It is a pleasant duty for one of us (S. R.) to express his best thanks to Mr. R. H. Adie for the valuable help received from him at the commencement of the research.

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Cambridge.

LXXII.—*Researches on Silicon Compounds and their Derivatives.* Part III. *The Action of Silicon Tetrabromide on Allyl- and Phenyl-thiocarbamides.* Part IV. *The Action of Ethyl Alcohol on the Compound* $(H_4N_2CS)_8SiBr_4$.

By J. Emerson Reynolds, M.D., F.R.S., Professor of Chemistry, University of Dublin.

Part III.

In a former paper (Trans., 1887, **51**, 202), I gave an account of the results obtained when silicon tetrabromide is made to act on the primary thiocarbamide in presence of benzene. It was shown that 8 mols. of the amide withdraw but 1 mol. of the tetrabromide from its solution, even after moderately prolonged heating with excess of it to the boiling point of benzene.

In this paper are described the results afforded by allyl- and phenyl-thiocarbamides when similarly treated.

The Action of Silicon Tetrabromide on Allyl-thiocarbamide.

The allyl-thiocarbamide used was prepared by the action of ammonia on the corresponding thiocarbimide. It was perfectly pure and dry, and readily fused under benzene to a clear liquid, since its melting point is 74°.

A quantity of the amide was fused under boiling benzene, in which it does not dissolve, and an equal weight of silicon tetrabromide gradually added. The mixture was then digested in a flask provided with a reflux condenser, and this treatment was continued for about two hours. The allyl-thiocarbamide gradually changed from a clear, mobile liquid to an opalescent, viscid mass, insoluble in benzene.

The latter, which contained much unaltered silicon tetrabromide at the end of the operation, was poured off and the mass digested with successive quantities of boiling benzene, in order to wash away any adherent tetrabromide.

The product, when cooled to the ordinary temperature, was a very viscid liquid, having a slight yellow colour. It held fine flakes of a white substance in suspension. The latter were partially removed by filtration under pressure at 100°, as at that temperature the liquid flows about as freely as pure glycerin does at the ordinary temperature.

It proved to be impracticable to wholly remove the white substance in this way, and, since the latter seemed to be a product of decomposition, another preparation was made exactly as above described, save that the excess of silicon tetrabromide was not allowed to act on the allyl-thiocarbamide for more than half an hour at the boiling point of benzene; but even under these conditions an opalescent product was obtained, and the benzene poured off had a distinct alliaceous odour.

Each preparation was found to contain silicon, bromine, and the proximate constituents of allyl-thiocarbamide. The following are the results of the analyses of No. 1 specimen,—the product obtained by the action of excess of tetrabromide during two hours; and of No. 2,—the corresponding product obtained by heating for only half an hour. The results are compared in the table with the calculated percentage composition of (A) an octothiocarbamide compound with silicon tetrabromide, and (B) the same substance *minus* one atom of sulphur:—

	Theory.		Found.	
	A.	B.	No. 1 product.	No. 2 product.
Si	2·19	2·25	1·95	1·83
Br.....	24·10	25·72	26·20	24·76
S	20·06	18·06	16·26	17·47
N	17·55	18·06	—	18·36

The conclusions drawn from these results were (1) that allyl-thiocarbamide quickly withdraws sufficient silicon tetrabromide from its benzene solution to form an octo-compound: but (2) that the product is decomposed by the continued action of excess of bromide, accompanied by greater or less loss of sulphur, according to the duration of the action, the white substance which rendered the viscid liquid somewhat turbid being, probably, one of the results of the secondary change. Such decomposition is analogous to that already traced analytically in the case of the primary thiocarbamide, though it is possible to prepare the nearly pure octo-compound of that body

in presence of benzene. The allyl-thiocarbamide, however, always afforded more or less decomposed products in presence of benzene, hence I discarded benzene altogether and found it easy to prepare any quantity of the allylic octothiocarbamide compound with silicon tetrabromide in the following way:—

9·28 grams (8 mols.) of perfectly dry allyl-thiocarbamide were poured into a pressure tube, which had been previously filled with dry carbon dioxide gas, 3·5 grams (or slightly more than 1 mol.) of pure silicon tetrabromide were then added, and the tube sealed. When the tube was heated in a current of steam, the amide melted and evidently combined with a portion of the tetrabromide, but much of the latter found its way to the bottom of the vessel and remained there under the layer of fused amide. By occasional agitation of the contents of the tubes, combination of the two substances was gradually effected in less than half an hour, and all but a minute trace of tetrabromide disappeared.

The product was a very pale-yellowish, perfectly transparent liquid at 100°, and about as viscid as pure glycerin is at ordinary temperature; when cold, the liquid became so viscid that the slowly moving liquid required two days to partially adapt itself to a reversed position of the tube.

This liquid is perfectly transparent and homogeneous; moreover, a specimen of it which has now been prepared for a considerable time (nine months) does not exhibit the slightest tendency to alteration. It is scarcely dissolved by benzene, but is readily dissolved and decomposed by alcohol and water.

The direct production of this remarkable compound thus confirms one of the conclusions arrived at by the study of the action of the benzene solution of silicon tetrabromide on allyl-thiocarbamide. An experiment was now made in order to ascertain whether an excess of the tetrabromide would attack the octo-compound.

4·64 grams of allyl-thiocarbamide (4 mols.) and 3·5 grams of silicon tetrabromide (1 mol.) were sealed up in a tube which had been previously filled with dry carbon dioxide gas. The tube was heated in a current of steam as before. Combination quickly took place, and the volume of tetrabromide diminished as the action proceeded. At first, a perfectly transparent viscid liquid was formed, from which the heavy tetrabromide readily subsided; but when sensibly half the latter had disappeared the whole became opalescent, and an hour's continued heating sufficed to render the liquid as turbid as the first product obtained when excess of tetrabromide was made to act for two hours on the amide in presence of boiling benzene. The tube was now heated at 100° for three days, but at the end of that time a very sensible quantity of tetrabromide remained free, while the

opacity and viscidity of the amidic compound had much increased; moreover, it completely solidified when cold. It is evident, then, that when excess of tetrabromide is allowed to act on the first product a further change is established which, probably, leads to the partial formation of a tetrathiocarbamide compound as well as other products which remain for detailed examination.

Hence, the primary product of the action of silicon tetrabromide on allyl-thiocabamide is the remarkably viscid liquid,

$$SiBr_4(SCN_2H_3C_3H_5)_8.$$

The similarity of this allylic compound in composition and some of its characters with that derived from the primary thiocarbamide indicates probably similarity of structure.

The Action of Silicon Tetrabromide on Phenyl- and Diphenyl-thiocarbamides.

Phenyl-thiocarbamide, or *thiocarbanilamide*, dissolves to a moderate extent in boiling benzene, though much quickly separates in crystalline condition if the temperature of the saturated solution be slightly reduced below its boiling point. In consequence of this solubility of the amide in hot benzene, it was hoped that silicon tetrabromide would precipitate an octothiocarbamide compound from the solution.

Silicon tetrabromide, mixed with benzene, was added hot to a boiling solution of phenylthiocarbamide in benzene. A yellowish, clotted mass quickly separated; this was repeatedly washed with hot benzene and allowed to cool; it then became a translucent, somewhat brittle solid at the ordinary temperature.

This substance proved on analysis to contain more of the thiocarbamide than was required for the octo-compound with silicon tetrabromide; the first preparation contained nearly 12 mols. of the amide for one of the tetrabromide. Further investigation showed that the octo-compound in precipitating carried with it more or less free amide, which could be only partially removed by boiling benzene, or changed by excess of tetrabromide; since either treatment speedily set up decomposition of the octo-compound, which latter appears to be even more prone to alteration than the analogous allylic product.

The following mode of operating, however, enabled me to obtain the octo-compound in nearly pure condition. 12·16 grams of pure and dry phenyl-thiocarbamide (8 mols.) were spread over the bottom of a small conical flask, which was heated on a water-bath. 3·5 grams of silicon tetrabromide (1 mol.) were poured over the amide so as to moisten it as completely as possible, and the mixture was heated to 100° for about half an hour in a slow current of dry carbon dioxide. It quickly became a viscid, opalescent mass, and continued in this con-

dition while over the water-bath. On removal from the latter, the flask was very carefully heated over the naked flame, when the substance almost immediately became a nearly transparent, yellowish liquid, which was more viscid than the allylic compound at the same temperature. On cooling, the new substance solidified to a hard, translucent, vitreous mass containing but few entangled, white particles.

Although the mode of preparation left no reasonable doubt as to the composition of this substance, the ratio of bromine to sulphur was determined in it and proved to be 1 : 2·035 or 4 : 8·14. It therefore contains $SiBr_4(SCN_2H_3C_6H_5)_8$.

It is slightly soluble in hot benzene, and is easily dissolved and decomposed by boiling anhydrous ethyl alcohol.

In another case it was found that obvious decomposition ensued when even a slight excess of tetrabromide was used above that employed in the experiment just described.

When *diphenyl-thiocarbamide* was warmed with silicon tetrabromide, combination also took place, and a yellowish, viscid liquid resulted, which solidified in a rather hard substance on cooling. The product dissolved in water and alcohol with evident decomposition, and generally resembled the monophenylic octothiocarbamide compound with silicon tetrabromide.

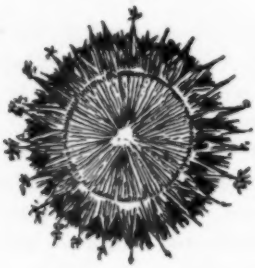
Part IV.—*The Action of Ethyl Alcohol on the Compound* $(SCN_2H_4)_8SiBr_4$.

It has been already mentioned that the octothiocarbamide silicon bromide is dissolved by anhydrous ethyl alcohol, and that it undergoes decomposition during solution. The products obtained in the course of this treatment include representatives of two new groups of thiocarbamide compounds, which will be described in this paper.

A large quantity of material for this branch of the inquiry was prepared in the following way :—100 grams of finely powdered thiocarbamide were treated as before with 90 grams of silicon tetrabromide in benzene solution. The product when thoroughly washed with benzene and dried, weighed 154 grams. 100 grams of thiocarbamide are capable of affording 157 grams of the octothiocarbamide compound, hence the conversion of the thiocarbamide into its silicon bromide compound was practically complete.

The product was then dissolved in boiling anhydrous ethyl alcohol; 900 c.c. were sufficient for the solution of the above weight of substance. A small quantity of light flocculent matter which separated, resembling gelatinous silica, was rapidly filtered off, and the alcoholic solution allowed to cool in a well-closed flask. Rapid cooling of

such a solution leads to the separation of small spheres like those of leucine, but which grow to a considerable size in the liquid. By slow cooling, however, beautiful stellate groups of fine silky crystals were formed, some of which closely resembled sea anemones in appearance. One of these groups, as seen from above, is shown in the annexed sketch.



When quite cold, the solution became an apparently solid felted mass of crystals. This material was drained by means of the filter-pump and washed with a little cold alcohol. The mother-liquor and washings afforded, on distilling off much of the alcohol, second and third crops of crystals, which latter were also washed, drained, and dried. The several crops were mixed, and then completely purified by repeated crystallisation from absolute alcohol.

The alcoholic distillates obtained in the course of this treatment were found to contain some ethylic thiocyanate, and a little bromide and sulphide. The residual alcoholic solution, from which the several crops of crystals had separated, was preserved for further examination, the results of which will be described later on.

A. *Examination of the Pure Crystals.*—These proved to be quite free from silicon, but contained much bromine and the constituents of thiocarbamide. The aqueous solution gave the galena reaction for thiocarbamide* freely, and was not coloured by ferric chloride.

The complete analysis of the compound led to the results stated below. I may mention, however, that the determination of hydrogen proved to be of exceptional difficulty, owing to the large proportion of sulphur, nitrogen, and bromine present.

I. 0·3545 gram, burned with lead chromate and copper gauze in front, gave 0·1561 gram of CO_2 and 0·1704 of H_2O.

Percentage of C = 12; of H = 5·34.

* "The Synthesis of Galena," by J. Emerson Reynolds. Trans., 1884, **45**, 162.

II. 0·3849 gram gave 0·1718 gram of CO_2 and 0·1848 of H_2O.
Percentage of C = 12·17; of H = 5·33.

*III. 0·3708 gram gave 0·1634 gram CO_2 and 0·1716 of H_2O.
Percentage of C = 11·98; of H = 5·17.

IV. 0·3561 gram gave, by Dumas's method, 95 c.c. of N at 10·8° and 750 mm.
Percentage of N = 31·24.

V. 0·3492 gram gave, by Will and Varrentrapp's method, 0·1092 gram of N.
Percentage of N = 31·27.

†VI. 0·6232 gram gave 1·441 gram of $BaSO_4$.
Percentage of S = 31·75.

VII. 0·7671 gram gave 1·776 of $BaSO_4$.
Percentage of S = 31·82.

VIII. 0·5041 gram gave 0·236 gram of AgBr.
Percentage of Br = 19·89.

IX. 0·466 gram gave 0·2186 gram AgBr.
Percentage of Br = 19·95.

The analytical data lead to the formula—

$$C_4H_{20}N_9S_4Br.$$

In the following table the calculated and experimental values are compared:—

	Calculated.	Found.		
C_4.....	11·94	12·00	12·17	11·98
H_{20}.....	4·97	5·34	5·33	5·17
N_9.....	31·34	31·24	31·27	—
S_4.....	31·84	31·75	31·82	—
Br.....	19·91	19·89	19·95	—

The new compound is therefore a derivative from 5 *mols. of thiocarbamide.*

The pure substance melts at 173—174°, and begins to decompose at 178—180°. It is easily soluble in boiling anhydrous alcohol; but is so much less soluble in the cold liquid that the hot saturated solution

* In this combustion, every precaution was taken to eliminate possible traces of carbon, hydrogen, and moisture from the materials. The lead chromate was first strongly heated in pure oxygen. The copper gauze was reduced in hydrogen, but was subsequently heated to redness in an atmosphere of pure and dry hydrogen.

† The sulphur and bromine determinations were made by improved methods, which afforded very concordant results, as seen above. An account of the processes will shortly be published.

becomes almost solid at the ordinary temperature. It is almost insoluble in ether, chloroform, and benzene. Water dissolves the compound, but at the same time partially decomposes it.

The composition and properties of this beautiful product led me to suspect that it might be regarded as $(H_4N_2CS)_4H_4NBr$, or $(H_5N_2CS)_4NBr$, consequently that its synthesis should be affected by the union of thiocarbamide with ammonium bromide; hence the following experiment was made:—

One gram of ammonium bromide was dissolved in as little absolute alcohol as possible, and the solution was added to a boiling and nearly saturated alcoholic solution of 3·04 grams (4 mols.) of pure thiocarbamide; the solution was again boiled for some time, and then allowed to cool in a flask. On standing, the contents of the flask solidified to a beautiful crystalline mass, identical in appearance with the product obtained from the silicon compound. The substance was drained from mother-liquor by the pressure pump, then purified by recrystallisation from alcohol, dried and examined.

The synthetic product melts at the same temperature as the original substance, and begins to decompose in the same way at 178—180°. Its other characters are the same. 0·2866 gram gave 0·135 AgBr = 20·04 Br. Theory for $(H_5N_2CS)_4NBr$ requires 19·91 of Br. There is therefore no doubt that the synthetic product is identical with that obtained by the aid of silicon bromide, and is a well-defined compound of a *tetrathiocarbamide* group, or is tetrathiocarbamidammonium bromide.

This result obviously raised the question whether analogous compounds could be obtained with other bromides, and considerable time was occupied in examining various products which were formed by the union of certain bromides, iodides, and chlorides, with 4 mols. of thiocarbamide. The following among a number of other similar compounds were obtained by the synthetic method, and will be described in detail in a separate paper. The formula of the original bromide is given at the head of the list for reference.

$(H_5N_2CS)_4NBr$, or
$(H_4N_2CS)_4H_4NBr$,
$(H_4N_2CS)_4H_4NI$,
$(H_4N_2CS)_4H_4NCl$,
$(H_4N_2CS)_4H_3(CH_3)NBr$,
$(H_4N_2CS)_4H_2(C_2H_5)_2NBr$,
$(H_4N_2CS)_4H(C_2H_5)_3NCl$,
$(H_4N_2CS)_4(C_2H_5)_4NBr$.

All the above compounds resemble the first in appearance and mode of crystallisation.

The converse question, that is, whether other amides than thiocarbamide would unite with ammonium bromide, was answered in the negative for the most part, as neither allyl-, phenyl-, diphenyl-, nor acetylphenyl-thiocarbamides united with the bromide under the conditions which led to the formation of the fine compound with the primary thiocarbamide. It will appear later on that this is a point of some theoretical interest, even though we should succeed in effecting union under other conditions.

The action of various metallic salts on tetrathiocarbamidammonium bromide have been examined, but the most interesting results were obtained with silver nitrate.

One milligram-molecule (0·402 gram) of the bromide was dissolved in 25 c.c. of very strong alcohol, and an alcoholic solution of silver nitrate (containing 0·01 gram of the salt in each c.c.) was gradually dropped into the bromide. A precipitate formed at each addition of the silver solution, but quickly redissolved until 17·5 c.c. had been added, that is, 0·175 gram of $AgNO_3$, or slightly more than 1 mgrm.-molecule. On continuing the addition of the silver solution, a granular white precipitate formed, and separated until 66 c.c. more (nearly 4 mols. in all) had been added. Near the end of the precipitation blackening occurred, owing to the formation of silver sulphide by secondary action.

In this case silver bromide was first formed by double decomposition with the new compound, and was momentarily precipitated, but the silver bromide was redissolved, in consequence of the formation of a soluble compound, $(H_4N_2CS)_2AgBr$, which can be crystallised out from the solution at this stage of the treatment.

The granular precipitate produced on the addition of silver nitrate to the argento-bromide solution is probably a mixture of monothiocarbamide compounds with silver bromide and nitrate.

The above results led to a general examination of the relations of silver haloïd compounds to thiocarbamide. It was found that solutions of thiocarbamide dissolved or acted upon silver bromide, chloride, iodide, cyanide, &c., directly, and the following, among other substances, were formed and analysed:—

$(H_4N_2CS)_2AgBr$,
$(H_4N_2CS)AgBr$,
$(H_4N_2CS)_2AgCl$,
$(H_4N_2CS)AgI$,
$(H_4N_2CS)_2AgCN$.

The results of the detailed study of the above and other similar compounds will form the subject of a separate communication. I may mention, however, that they have afforded the clue required for

the interpretation of some obscure facts recorded in one of my earlier papers on the metallic compounds of thiocarbamide.

B. *Examination of the Residual Liquid from Crystals of the Tetrathiocarbamide Compound.*—This has led to the recognition of an interesting *trithiocarbamide* derivative, the first of its class.

The liquid from which successive quantities of the crystals were separated, as already described, was reduced by distillation to 180 c.c., which had the sp. gr. 1·108.

When this yellowish residual liquid was treated with twice its volume of anhydrous ether, the mixture separated in two layers. The heavier layer was removed, shaken up with fresh quantities of ether, and the ethereal solutions were mixed and preserved for further examination, as the ether was found to hold an ethylic silicate in solution.

The heavy liquid, separated from ether, slowly deposited a considerable quantity of short, transparent, prismatic crystals. These closely resembled *dithiocarbamidethyl bromide* in appearance, and, like the latter, afforded a fine yellow precipitate of *lead mercaptide* when the solution was treated in the cold with alkaline lead tartrate. On boiling with excess of the lead solution, the galena reaction was also obtained.

The compound, when purified by three crystallisations from anhydrous alcohol, was carefully dried and analysed. Its formula proved to be $C_5H_{10}N_6S_3Br_2$.

The following are the data obtained:—

I. 0·484 gram of substance gave 0·2118 gram of H_2O and 0·2535 of CO_2.
Percentages of C = 14·28; of H = 4·86.

II. 0·4 gram gave 0·164 of H_2O and 0·211 of CO_2.
Percentages of C = 14·38; of H = 4·55.

III. 0·3525 gram gave 0·4935 of Pt.
Percentage of N = 20·17.

IV. 0·7461 gram gave 0·6675 of AgBr.
Percentage of Br = 38·07.

V. 1·4775 gram gave 2·484 of $BaSO_4$.
Percentage of S = 23·11.

VI. 0·35 gram gave 0·589 of $BaSO_4$.
Percentage of S = 23·13.

The percentage composition of the substance is—

	Theory.	Found.	
C_5	14·29	14·28	14·38
H_{20}	4·76	4·86	4·55
N_6	20·00	20·17	—
S_3	22·85	23·11	23·13
Br_2.....	38·08	38·07	—

The experimental values, therefore, fairly agree with those calculated from the formula. The elements nitrogen, sulphur, and bromine, when present together in large proportions in a compound, as in the present instance, render the precise determination of hydrogen somewhat uncertain; hence in the case of a substance which has so high a molecular weight (420) as that in question, analysis alone cannot decide between such expressions as H_{19} and H_{20}, for the probable number of hydrogen-atoms in the molecule. But the choice in this instance lies rather between H_{16} and H_{20}, as any intermediate expression would present greater theoretical difficulty than either. Analysis readily decides in favour of the higher value, viz.:—

	Calculated for H_{16}.	Calculated for H_{20}.	Found (mean).
Percentage of hydrogen..	3·846	4·762	4·705

Moreover, the formula deduced best accords with the mode of derivation of the compound, and with the following facts which indicate its nature.

The new substance readily affords lead mercaptide, or mercaptan itself (ethyl thiohydrate) when boiled with caustic potash, consequently it contains the ethyl-group directly united with sulphur. It also easily yields up bromine to alkalis. In so far as it is analogous to the dithiocarbamidethyl bromide,

$$\begin{matrix} H_4N_2CS\cdot C_2H_5 \\ | \\ H_4N_2CS\cdot Br \end{matrix},$$

which acts in a similar manner, and is therefore a sulphinic compound of ethyl bromide also. Further, the composition of the body, and the fact that it gives the galena reaction on heating for some time with alkaline lead solution, indicate the presence of three groups derived from 3 mols. of thiocarbamide. These facts point to the following as the formula for the compound: $(H_5N_2CS)_3BrC_2H_5Br$.

If this be confirmed by synthesis, it will materially strengthen the evidence of the unsymmetrical structure of the thiocarbamide itself, and even suggest an expression for the latter; but it would be premature to discuss this subject at the present stage of the inquiry.

C. *The Ethereal solution* that separated from the liquid which afforded the compound last described, was distilled from the water-bath as long as any ether passed over. The residue, which was a thick liquid, was poured into a tube and hermetically sealed, as it was found to rapidly hydrate and gelatinise on exposure to air. After standing for three months, a mixture of crystals had separated, consisting of the two thiocarbamide-derivatives (which are not quite insoluble in ether containing alcohol) and the usual gelatinous product from diethylic silicate.

The investigation of the action of ethyl alcohol on the compound $(H_4N_2CS)_3SiBr_4$ has therefore shown—(1) that ethyl bromide, thiocyanate, and silicate are formed; (2) that but one of the thiocarbamide-groups undergoes actual resolution; (3) that the remaining 7 mols. of the amide afford the tri- and tetra-thiocarbamide compounds described.

Only two classes of thiocarbamide products have hitherto been known, namely, those derived from 1 mol. or 2 mols. of the amide; but it has been shown in this paper that 3 and even 4 mols. can unite in forming more highly condensed compounds under the influence of silicon tetrabromide and even less powerful agents.

Ethyl alcohol also dissolves and decomposes the compounds of allyl- and phenyl-thiocarbamides with silicon tetrabromide, but the products have not been examined in detail.

I desire to acknowledge the valuable assistance received in the analytical part of the work recorded in this paper from my friend and former pupil, Emil A. Werner, F.C.S.

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LXXIII.—*The Heat of Dissolution of Substances in different Liquids, and its bearing on the Explanation of the Heat of Neutralisation, and on the Theory of Residual Affinity.*

By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College.

A short time ago, I drew the attention of the Society to the fact that the thermal results of neutralisation proved the existence of an equality represented by—

$$M,R,aq - M',R,aq = M,R',aq - M',R',aq, \qquad (1)$$

in which M and R represent metallic and non-metallic radicles, and I pointed out that, unless we could assume the existence of a similar equality as regards the constituent parts of these terms, namely, the heat of formation of the salt molecules from the atoms—

$$M,R - M',R = M,R' - M',R',$$

and the heat of dissolution of these molecules in water—

$$MR,aq - M'R,aq = MR',aq - M'R',aq,$$

an assumption which I regarded as most improbable, these two constituent actions must be integral parts of one and the same reaction, namely, the perfect saturation of the affinity of the radicles M or R; and, that, as the first action is chemical, so also must be the second one, the dissolution of the salt molecules (Trans., 1887, 593). My explanation of the facts of the case was subsequently reproduced almost *verbatim* by Dr. Nicol in a paper read before the British Association in 1887 (see *Chem. News*, **56**, 162), and he suggested, though on very weak grounds, in my opinion,* that this equality did hold good of each of the two constituent actions. The paramount importance of the conclusions drawn from the heat of neutralisation renders it necessary to examine any possibility, however improbable, of its being interpreted in a sense consistent with the so-called physical theory of solution.

* The grounds were that a few very imperfect determinations seemed to show that the difference in the extent to which the vapour-pressure of water is lowered by the addition of salts of two different acids is independent of the nature of the metal present. But even if further experiments prove this to be the case, we should still have to prove the proportionality between the lowering of the vapour-pressure and the heat of dissolution (see *Chem. News*, **56**, 191).

It appeared that the possibility of the equation—

$$MR,aq - M'R,aq = MR',aq - M'R',aq$$

(which represents, be it noted, the heat of combination of *single molecules* with excess of water, not the heat of dissolution of masses of the solid salts), holding good, might be settled in the following manner.

During the dissolution of a substance, three forces must come into operation, whether these forces be chemical or physical:—(1) the attraction of salt molecule for salt molecule; (2) the attraction of the molecules of the solvent for each other; (3) the attraction of the salt molecules for the solvent molecules. The first of these is independent of the nature of the solvent, and the second is independent of the nature of the dissolved substance, the third only is dependent on both substances.

Now, by taking a sufficient excess of the solvent we shall have the attraction of salt molecule for salt molecule practically entirely overcome; and we shall also have the attraction of the molecules of the solvent for each other overcome to the same extent whatever salt be dissolved in it. This is obviously true when the proportion of the solvent is infinite, for then, not only will the dissolved molecules be entirely separated from each other, but the solvent molecules will be less united with each other than they are when no dissolved substance is present by only an infinitesimally small amount, which infinitesimally small amount will differ according to the salt dissolved by a still more infinitesimal amount. We cannot, of course, use an infinitely large proportion of solvent, but, by taking some 500—1000 mols. of it we obtain values which, as I will show, can differ by but very little from those referring to infinite dilution.

Now let the heat evolved in the satisfaction of the various attractions concerned be $(MR)c$, $(M'R)c$, &c., for the attraction of the salt molecules for each other; let w and a represent that due to the combination of the solvent molecules with each other, where the solvent is water and alcohol respectively, and let $(MR)w$, $(M'R)w$, $(MR)a$, $(M'R)a$, &c., represent the heat of combination of the various salt molecules with the two solvents; then the heat evolved in the dissolution of the solid MR in infinity of water will be $[-(MR)c - w + (MR)w]$, and in alcohol, $[-(MR)c - a + (MR)a]$, and so on with the other salts, M'R, MR', &c.

On the physical theory of solution the same relation must exist between the heat of dissolution of various salt molecules in alcohol as in water; if with water, we have—

$$MR,aq - M'R,aq = MR',aq - M'R',aq,$$

or, in the above notation—

$$(MR)w - (M'R)w = (MR')w - (M'R')w,$$

so, with alcohol, we must have—

$$(MR)a - (M'R)a = (MR')a - (M'R')a,$$

which two equations may be combined into—

$$(MR)(w-a) - (M'R)(w-a) = (MR')(w-a) - (M'R')(w-a), \qquad (2)$$

and the observed heat of dissolution of the various solid salts in water and alcohol must show the following relations:—

Diss. of solid MR in water	−	Diss. of solid MR in alcohol.
$[-(MR)c - w + (MR)w]$	−	$[-(MR)c - a + (MR)a]$
− Diss. of solid M′R in water	+	Diss. of solid M′R in alcohol.
$-[-(M'R)c - w + (M'R)w]$	+	$[-(M'R)c - a + (M'R)a]$
= Diss. of solid MR′ in water	−	Diss. of solid MR′ in alcohol.
$=[-(MR')c - w + (MR')w]$	−	$[-(MR')c - a + (MR')a]$
− Diss. of solid M′R′ in water	+	Diss. of solid M′R′ in alcohol.
$-[-(M'R')c - w + (M'R')w]$	+	$[-(M'R')c - a + (M'R')a]$,

because this equation simplifies into (2).

This would, moreover, hold good even if the alcohol contained water; for, in such a case, $(MR)c$ would still have the same value, and for the complete separation of the particles of this mixed liquid we should have a', which would cancel out in the same way as a does; while, for the results of the action of the salt molecules on those of the dilute alcohol, containing $1/x$th of its weight of water, we should have $(1 - x)(MR)a + x(MR)w$, instead of $(MR)a$, since (still according to the physical conceptions of solution) the salts would in each case exert their influence on the alcohol and water (in the dilute alcohol) in direct proportion to the relative masses in which these were present, and our equation would still simplify into equation (2).

The determination of the heat of dissolution of the four suitable salts in water and alcohol became, therefore, necessary. The salts selected were the anhydrous chlorides and nitrates of lithium and calcium, but in addition to these, other salts were also examined for purposes to be mentioned below.

The determinations in alcohol were attended with considerable difficulties. It was found that many of those salts which were said to dissolve in alcohol did so to a scarcely appreciable extent when the alcohol was anhydrous, or, at any rate, not in sufficient quantities for calorimetric purposes. In the case of several of the salts which were

eventually taken, over 1000 mols. of the alcohol had to be used for each molecule of the salt, and, even then, the dissolution took a very considerable time, necessitating the application of a large correction for the loss of heat by cooling during the determination. In one or two cases, the salt was not entirely dissolved, and the amount which had dissolved had to be subsequently estimated in the liquid. Owing to the comparatively high molecular weight and small density of alcohol, the volume of this liquid, which should be taken to give the same molecular proportions between the solvent and salt as in the case of water, should be four times as great as with water, but for economical reasons the volume of 600 c.c. generally used was reduced to 270 c.c., and consequently the weight of salt taken was very small, often but a fraction of a gram, so that the observed evolution of heat had to be multiplied by some hundreds to give the so-called molecular heat of dissolution. Most of the salts, moreover, are of an extremely hygroscopic nature, and some of them, such as $ZnCl_2$, $CaBr_2$, and CaI_2, especially this last, could not be obtained in an anhydrous condition without experiencing a certain amount of decomposition. But the chief source of error in such determinations is that the rate of cooling is at least 10 times greater than in the case of water, owing to the volatility of the alcohol.

The results are given in Table I (p. 875). For the open calorimeter holding 270 c.c., used in the earlier determinations, a calorimeter holding 600 c.c., and covered with a thin copper lid with an opening in it for the introduction of the salt, was substituted in the later determinations, the rate of cooling being thereby greatly reduced.

In the case of the determinations with the chlorides and nitrates of lithium and calcium, the later determinations gave considerably higher results: the difference is greater than can be accounted for by the errors in the thermometric measurements, and is probably due to the fact that in the earlier determinations, the tubes in which the salts were weighed out before dissolution had not, as far as I can remember, been specially heated immediately before the introduction of the salt, and the 2 or 3 mgrms. of moisture adhering to the surface of the glass would have produced a considerable amount of hydration of the small quantity of salt taken. This explanation is rendered all the more probable by the fact that with the less hygroscopic sodium iodide the difference is scarcely appreciable, and with the non-hygroscopic mercuric chloride there is no difference at all. At any rate, the earlier and later determinations are consistent in themselves, and whichever are taken for the purposes of our equation, the result obtained is practically the same.

The alcohol taken was dehydrated by exposure for a week or two in a vacuum over freshly burnt lime.

In this and the subsequent tables—

w = the weight of salt taken,
W = that of the solvent,
c = the heat capacity of the solvent,
$w''c'' + w'c'$ = the heat capacity of the solution and apparatus,
$(t' - t)°$ = the corrected rise of temperature,
D^m = the heat of dissolution for one gram-molecular proportion of the salt,

and the probable error given in the last column is the difference which would have resulted from an error of 0·002° in the determination of the rate of cooling per minute: half this amount only is taken in calculating the probable error in the later determinations.

The heat capacity of the solution is taken as being equivalent to the sum of those of the solvent and the dissolved salt.

In the case of the three later determinations with calcium chloride, some variation is noticeable: this is probably due to the different amounts of solvent taken, and in taking the mean it will be well to omit the one with only 440 C_2H_6O, and take the other two, which do not differ from each other by more than the amount due to the error of reading the thermometer.

The determination of the heat of dissolution of these same salts in water is given in Table II, where the results are compared with those obtained by Thomsen. With these they agree very well, except in the case of CaI_2, where the specimen used by myself was known to be considerably decomposed. With $CaCl_2$, $Ca(NO_3)_24H_2O$, NaI, $Na(C_2H_3O_2)$, and $Mg(NO_3)_26H_2O$ my results are appreciably higher than Thomsen's, whereas with $CaCl_26H_2O$, LiCl, $CaBr_2$, $ZnCl_2$ (the last two being both known to be partly decomposed) the reverse is the case. Whether evolution or absorption of heat occurs, those results which give the highest numbers are probably the most correct.

The experimental error is here much less than in the case of alcohol, generally about $\pm$ 5 cal.

Taking, now, the values here obtained (the later and more accurate determinations with alcohol being alone considered), and substituting them in our equation above, we get—

Diss. of solid $CaCl_2$ in water.	−	Diss. of solid $CaCl_2$ in alcohol.
18,723	−	17,555
−Diss. of solid 2LiCl in water.	+	Diss. of solid 2LiCl in alcohol. =
− 16,312	+	23,486 =
Diss. of solid $Ca(NO_3)_2$ in water.	−	Diss. of solid $Ca(NO_3)_2$ in alcohol.
3,943	−	8,710

− Diss. of solid $2LiNO_3$ in water.	+	Diss. of solid $2LiNO_3$ in alcohol.
− 662	+	9,310

or 8,342 = 3,881.

numbers showing a difference of 4461 cal., where, if Dr. Nicol's view be correct, there should be equality. I do not feel sure whether according to his view an equivalent of the calcium salts should be compared with a double equivalent of the lithium salts as above, but if not the discrepancy becomes still greater, giving us

$$4755 = -443$$

for the two sides of the supposed equation.

For the absolute validity of our argument, the proportion of solvent should, as I have already mentioned, be infinite, but the further dilution of these very dilute solutions gives such feeble calorimetric results that the values obtained for infinite dilution would differ by very little from those taken here. By performing a series of experiments with different proportions of solvent, and plotting out the results against the percentage instead of the molecular composition of the solution, we get a curve which can easily be extended to the zero point, that is, to infinite dilution. This has been done with series of determinations which I have made with calcium nitrate and chloride in water, and thus it was found that infinite dilution of $Ca(NO_3)_2400H_2O$ would absorb 120 cal., and of $CaCl_2400H_2O$ would evolve 550 cal. If we admit a possible error of 350 cal. from this source in each of the values used in our equation, and that the sign of this error is always of a character favourable to rendering the two sides equal, we should obtain for the sum of the errors only 2800 cal., which would still leave an irreconcilable difference of 1661 cal.; it is, however, far more probable, if not, indeed, certain, that the sign of the corrections would be the same with each salt whether water or alcohol were the solvent, and in this case they would exactly or nearly counterbalance each other, according as they were exactly or nearly the same in value with the two solvents.

Though it would be advisable before drawing too rigid a conclusion to examine other sets of salts, still, as it does not appear possible to obtain any other suitable sets, we must take these results as showing conclusively, as far as they go, that no such relationship exists between the heat of dissolution of salts in water and in alcohol as would exist if the equation

$$MR,aq - MR',aq = M'R,aq - M'R',aq$$

were true; and, hence, that this so-called physical explanation of the thermal results of neutralisation is opposed to experimental evidence.

According to my explanation of the heat of neutralisation, the residual affinity of one of the radicles composing any salt molecule becomes entirely saturated when it is dissolved in excess of water, and it appeared probable at first sight that, since the amount of this residual affinity is independent of the nature of the solvent, the heat of dissolution of a salt must be the same whatever the solvent be. The other determinations given in Tables I and II were made with a view of investigating this point. The general results are collected in the following table, the numbers in brackets referring to the order of magnitude of the quantities.

Salt.	In water.	In alcohol.	Difference.
$CaBr_2$	(1) 23,293	(1) 21,471	−1,822
$CaCl_2$	(2) 18,723	(3) 17,555	−1,168
CaI_2	(3) 15,937 (?)	(2) 19,833 (?)	+3,896
$ZnCl_2$	(4) 15,220	(5) 9,767	−5,453
$LiCl$	(5) 8,156	(4) 11,743	+3,587
$Na(C_2H_3O_2)$	(6) 3,948	(9) 1,274	−2,674
$Ca(NO_3)_2$	(7) 3,943	(6) 8,710	+4,767
NaI	(8) 1,404	(8) 4,587	+3,183
$LiNO_3$	(9) 331	(7) 4,655	+4 324
$HgCl_2$	(10) −2,116	(11) 0	+2,116
$CaCl_26H_2O$	(11) −4,251	(13) −2,563	+1,688
$Mg(NO_3)_26H_2O$	(12) −4,547	(10) 936	+5,483
$Ca(NO_3)_24H_2O$	(13) −8,354	(12) −1,835	+6,419

That the heat of dissolution is the same in the two cases is at once disproved. There is a rough similarity in order of magnitude in the two series, but beyond this no other connection is noticeable. The difference between the heat of dissolution in the two liquids ranges between −5500 and +6400 cal., though with alcohol the numbers obtained are generally the higher of the two. To these we may append the following:—

$ZnCl_2$ in water	15,220	cal.
„ NH_4Cl sol.....	15,091	„
„ KCl „	14,895	„
$HgCl_2$ in water.....	−2,116	„
„ NH_4Cl sol.....	−1,623	„

where the values, though more nearly the same than in the case of alcohol, are certainly not identical.

On further consideration, however, it does not appear that the heat of dissolution of a salt should, according to my views, be independent of the nature of the solvent.

The equation—

$$M,R,aq - M,R',aq = M',R,aq - M',R',aq,$$

holds good (1) if *one* of the radicles only in each case be saturated by the solvent, and (2) if this radicle be saturated by the *free* affinity of the solvent. If the heat evolved in saturating it were counterbalanced in part, and to different extents in different cases, by any alteration in the force with which the molecules of the solvent were united with each other, or with which the atoms are combined together in the molecule, or if any of the residual affinity of *both* radicles of the salt were saturated by the solvent, then the equation would no longer hold good. In the case of water we are dealing with a substance composed simply of one metallic and one non-metallic substance, the atomic constitution of which is very simple and very stable, and such a solvent may well act so as to fulfil the two necessary conditions above mentioned,* whereas other less simple and less stable solvents would not do so. This appears, at any rate, to be the case with alcohol.

It is impossible with the means at our disposal to get other solvents as simple as water in order to prove the truth of this view, but it seemed probable that some approach to constancy in the heat of dissolution might be obtained by simplifying the substance dissolved instead of the solvent. By taking an elementary substance instead of a salt, we do away with the possible saturation of the two different radicles, and the second of the above-mentioned conditions will then be the only one to be fulfilled in order to produce this constancy.

Table III contains the results obtained on dissolving iodine, bromine, and sulphur in various liquids, the numbers in columns 3 and 8 referring to gram-atomic proportions of the substances.

Many of these liquids being more volatile than alcohol, the difficulties of the determinations were proportionately greater, and although the 600 c.c. calorimeter with its cover was used in every case, the cooling produced by evaporation was very great. The iodine used had been precipitated from an alcoholic solution and dried by exposure in a vacuum, this treatment rendering it more finely divided and hence more easily soluble. The bromine, however, was only a commercially pure specimen. In dissolving the latter, it was enclosed in a sealed bulb, which was eventually broken under the surface of the liquid. To break such a bulb at a particular moment in a liquid which is being continually stirred, in which there is suspended a very delicate thermometer, and which is contained in a

* Some of the many exceptions to the constancy of the heat of neutralisation are, no doubt, due to these conditions not being always fulfilled even in the case of water.

calorimeter supported on points only, is not a very simple operation. The following apparatus was devised for the purpose, and found to act well:—The bulb was kept in position at the bottom of the liquid by means of a small inverted platinum cone with jagged edges fixed on to a long platinum rod which extended to the top of the calorimeter, and which was united by a vulcanite connection to a longer brass rod, this brass rod being held by means of a screw and socket to an arm projecting from the jacket of the calorimeter. As soon as the temperature was constant, the screw was loosed, and a tap on the top of the brass rod was sufficient to drive the cone on to the bulb and break it. It is well to make the bottom of the bulb somewhat concave, and place under it a spiral of thick platinum wire with a projection in the middle, the projection getting driven against the concave bottom of the bulb facilitates its being broken. A false bottom, consisting of a disc of very open platinum gauze, is placed in the calorimeter so as to cover the bulb and prevent the broken glass from being driven against the thermometer by the stirrer.

The present experiments were only intended to be preliminary in their character. The solvents used, though commercially "pure," were far from being so in reality; their heat capacity (specific heat), moreover, is known with no degree of certainty: yet the results obtained are eminently suggestive. With iodine, the heat of dissolution for 126·54 grams is as follows:—

In benzene	−3057 cal.
„ chloroform	−3007 „
„ carbon tetrachloride	−2891 „
„ carbon disulphide	−2504 „
„ ammonium chloride sol..	−1538 „
„ alcohol	−857 „
„ ether	−768 „
„ potassium iodide sol. ...	−546 „

With the first three solvents, none of which contain oxygen, the heat of dissolution is practically constant within the limits of experimental error; with carbon disulphide, there is an appreciable rise in the heat developed, which attains still greater proportions in all the solvents containing oxygen, alcohol and ether giving nearly the same results. The amount of iodine dissolved in the ammonium chloride solution was so small that the value obtained is only a rough approximation.

With bromine (79·76 grams), where only a small number of solvents could be tried, the results are—

In water	−754 cal.
„ chloroform.....	−323 „
„ carbon tetrachloride....	−265 „
„ carbon disulphide.....	−7 „
„ water (Thomsen)	+539 „
„ potassium bromide sol. .	+1090 „

showing the same fact as with iodine, that the sulphurised solvent gives slightly higher values, and the oxygenated ones give considerably higher values, than the others. The results with water, however, are exceptional in this respect. This may be due to moisture or impurity in the bromine, and it is noticeable that my value differs considerably from Thomsen's, which comes in the position we should expect it to from the results with iodine.* With benzene and ether, the values obtained are much higher than in the other cases, for here we get ordinary chemical actions occurring.

With sulphur (octohedral), the values for 31·98 grams are as follows:—†

In ether	−1499 cal.
„ chloroform	−697 „
„ benzene	−690 „
„ carbon tetrachloride....	−624 „
„ carbon disulphide.....	−469 „

Here, as in the case of iodine, the chloroform and benzene give identical numbers, and, as in the cases of both iodine and bromine, the values with carbon tetrachloride are slightly smaller, and those with carbon disulphide considerably smaller. The results with ether, however, are different from those in the case of the halogens, showing a larger instead of a smaller absorption of heat than with the other solvents, and this difference is, I think, far too great to be accounted for by experimental error due to the great rate of cooling and the smallness of the quantity of sulphur dissolved.

Considering the very large experimental error in determinations with these volatile liquids, the impurity of the majority of them,‡ and

* Thomsen, however, gives no details as to the preparation of his bromine, or as to the method by which he obtained his results. With such a volatile liquid, special precautions must be taken to prevent the bromine vaporising and giving the heat of dissolution of bromine vapour, a quantity which would be considerably greater than that of liquid bromine. Berthelot (*Méc. Chim.*, 1, 511) misquotes Thomsen's number as applying to gaseous bromine.

† Alcohol was found to dissolve sulphur in proportions too small (0·075 p. c. at 18°) to render a determination with it practicable.

‡ The solution of iodine in carbon bisulphide and benzene showed signs of considerable action after being kept for six days, so also did the solution of bromine in chloroform.

TABLE I.—*Heat of Dissolution of Various Salts in Alcohol and other Liquids at 18° ± 0·01. Heat capacity of Alcohol*

TABLE I.—*Heat of Dissolution of Various Salts in Alcohol and other Liquids at* 18° ± 0·01. *Heat capacity of Alcohol* = 0·597.

Salt.	*w*.	Solvent.	W.	$w''c'' + w'c'$.	$(t' - t)°$.	D^m.		Probable error.
		Earlier Determinations.						
$CaCl_2$	0·549	$930C_2H_6O$	214·39	122·94	0·6392	15,838		±200
$CaCl_26H_2O$	2·643	400 „	„	123·69	−0·2481	−2,536		±140
$Ca(NO_3)_2$	1·066	750 „	„	123·12	0·3992	7,548		±500
$Ca(NO_3)_24H_2O$	2·855	400 „	„	123·61	−0·1754	1,835		±100
$CaBr_2$	0·535	1740 „	„	122·91	0·4686	21,471		±600
CaI_2	0·439	3270 „	„	122·88	0·2418	19,833		±1000
$ZnCl_2$	1·908	330 „	„	122·90	1·1160	9,767		±2220
LiCl	0·382	500 „	„	122·96	0·7582	10,344		±130
$LiNO_3$	1·579	200 „	„	123·33	0·6065	3,262		± 65
NaI	1·007	750 „	„	122·94	0·2266	4,137		±150
$HgCl_2$	3·168	400 „	„	„	0	0		±74
$Mg(NO_3)_26H_2O$	3·331	360 „	„	123·75	0·0986	936		±75
$NaC_2H_3O_2$	0·338	1100 „	„	122·90	0·0428	1,274		±420
$ZnCl_2$	11·502	$3NH_4Cl400H_2O$	—	607·69	2·0114	15,091		—
„	11·354	$3KCl400H_2O$	—	603·06	2·0678	14,895		—
$HgCl_2$	8·529	$7·5NH_4Cl1050H_2O$	—	607·69	−0·0842	−1,623		—
„	11·631	$6KCl800H_4O$	—	603·06	−0·0953	−1,336		—
		Later Determinations.						
$CaCl_2$	2·6140	$440C_2H_6O$	476·76	295·71	1·3784	17,274		±43
„	1·9350	600 „	„	295·84	1·0346	17,502	17,555	±114
„	1·6387	700 „	„	295·85	0·8814	17,607		±150
$Ca(NO_3)_2$	2·3312	700 „	„	296·01	0·4190	8,708	8,710	±84
„	2·2419	750 „	„	295·99	0·4031	8,711		
LiCl	0·6201	700 „	„	295·67	0·5811	11,743		±130
$LiNO_3$	1·8359	390 „	„	295·92	0·4173	4,635	4,655	±47
„	1·8939	380 „	„	295·93	0·4342	4,675		
NaI	2·954	520 „	„	295·99	0·3062	4,587		±46
$HgCl_2$	2·928	940 „	„	296·00	0	0		±60

TABLE II.—*Heat of Dissolution of Various Salts in Water at* 18° ± 0·01. *Water* = 601·173 *grams. Water Equivalent Apparatus* = 8·28 *grams.*

Salt.	w.	Solvent.	$(t' - t)°$.	$w''c'' + w'c'$.	D^{m}.		Values according to Thomsen.
$CaCl_2$	8·990	$400H_2O$	2·4904	610·24	18,705	18,723	17,410
„	8·802	„	2·4429	„	18,740		
$CaCl_26H_2O$	18·631	„	−0·5892	619·46	−4,279		
„	19·156	„	−0·5995	619·73	−4,236	−4,251	−4,340
„	18·067	„	−0·5664	619·20	−4,239		
$Ca(NO_3)_2$	14·687	„	0·5581	610·24	3,940	3,940	3,950
„	14·842	„	0·5647	610·35	3,945		
$Ca(NO_3)_24H_2O$	20·803	„	−1·1698	616·53	−8,354	−8,354	−7,250
„	19·796	„	−1·1142	616·23	−8,354		
$CaBr_2$	8·705	$800H_2O$	1·9351	610·24	23,293		24,510
CaI_2	12·157	„	1·0836	„	15,937		27,690
$ZnCl_2$	10·833	$400H_2O$	1·9921	„	15,220		15,630
LiCl	7·118	$200H_2O$	2·2449	„	8,156		8,440
$LiNO_3$	11·098	„	0·0872	„	331		300
NaI	24·836	„	0·3820	„	1,404		1,220
$HgCl_2$	11·573	$800H_2O$	−0·1483	„	−2,116		−3,300
$Mg(NO_3)_26H_2O$	21·858	$400H_2O$	−0·6278	619·61	−4,547		−4,220
$Na(C_2H_3O_2)$	See Trans., 1887, 315.	$200H_2O$	—	—	3,948		3,870

TABLE III.—*Determination of the Heat of Dissolution of Iodine, Bromine, and Sulphur in various Liquids at* $18° \pm 0·1$.

Substance.	w.	Solvent.	w'.	c.	$w''c'' + w'c'$.	$(t' - t)°$.	D^a.
Iodine	3·0230	$440C_2H_6O$	476·76	0·597	295·71	−0·0692	−857
,,	3·2484	$390CS_2$	762·11	0·239	194·24	−0·3309	−2504
,,	2·5857	$370CHCl_3$	897·4	0·234	221·94	−0·2769	−3007
,,	1·8941	$400(C_2H_5)_2O$	434·37	0·537	245·03	−0·2486	−768
,,	1·4085	$600C_6H_6$	530·1	0·436	243·06	−0·1403	−3057
,,	2·0102	$350CCl_4$	860·1	0·201	184·73	−0·2486	−2891
,,	7·9532	$3·8KI555H_2O$	630·0	0·868	556·31	−0·0618	−546
,,	0·2429	$124NH_4Cl15,500H_2O$	604·09	0·952	584·51	−0·0505	−1538
Bromine	0·8488	$2700H_2O$	511·86	0·999	519·69	−0·0155	−754
,,	1·6281	$8·5KBr1400H_2O$	534·35	0·958	519·43	+0·0428	+1090
,,	2·8991	$220CS_2$	600·35	0·239	153·08	−0·0016	−7
,,	1·8710	$300CHCl_3$	764·55	0·234	189·07	−0·0401	−323
,,	2·2591	$160CCl_4$	707·75	0·201	152·47	−0·0492	−265
,,	1·7450	$230(C_2H_5)_2O$	367·60	0·537	208·00	+0·4331	+4118
,,	1·7684	$270C_6H_6$	460·20	0·436	209·37	+1·5956	+15,068
Sulphur	5·140	$48CS_2$	584·00	0·239	152·20	−0·4954	−469
,,	4·235	$35CCl_4$	702·10	0·201	153·58	−0·5366	−624
,,	4·419	$40C_6H_6$	413·50	0·436	192·81	−0·4942	−690
,,	0·743	$200(C_2H_5)_2O$	368·10	0·537	210·07	−0·1658	−1499
,,	3·204	$60CHCl_3$	672·2	0·234	169·56	−0·4121	−697

our imperfect knowledge of their heat capacity, the results are strongly in favour of the conclusion that the heat of dissolution of an elementary body in a solvent of simple constitution is a constant quantity, as must be the case if the heat evolved is due to the complete saturation of residual affinity.*

I may take the present opportunity of mentioning one point of interest in connection with the heat of neutralisation. The equation (1) (p. 865) applied to the case of any two alkalis gives us—

$$K,OH,aq - Na,OH,aq - K,Cl,aq + Na,Cl,aq = 0,$$

showing that K may be represented by hydrogen as well as other radicles. In the case where two different acids are treated with the same base, we find that M may be represented by hydrogen as well as by other metals; but if the hydrogen is associated with hydroxyl the constancy no longer obtains. The neutralisation of an acid by an alkali gives—

$$H,OH,aq - Na,OH,aq - H,Cl,aq + Na,Cl,aq = 13,750 \text{ cal.}$$

instead of 0. From which we must conclude that the heat of formation of H_2O from H and OH, and the subsequent union of the various H_2O molecules thus formed into aggregates, is greater by 13,750 cal. than the heat of formation of the other bases (K,OH), and the union of these bases with excess of water. As the heat of formation of the water aggregates from the fundamental molecules cannot be greater than the heat of volatilisation of the water, some 10,000 cal. at 18°, it is evident that the heat of combination of OH with H is several thousand cal. greater than it is with any other metallic atom.

* Berthelot (*Méc. Chim.*, 1, 546) gives some approximate values for the heat of dissolution of naphthalene (128 grams) in alcohol, ether, and acetic acid, which are confirmatory of the constancy observed by me; they are: −3700, −3900, and −4,300 cal. respectively.

LXXIV.—*The Constitution of the Terpenes and of Benzene.*

By William A. Tilden, D.Sc., F.R.S.

The idea that turpentine and lemon oils consist of a hydride of cymene is due to Oppenheim (*Ber.*, **5**, 94 and 628). This view has been supported by Kekulé (*Ber.*, **6**, 438), and very generally adopted down to the present time. Nevertheless, I believe it to be inconsistent with many of the most prominent characteristics of these hydrocarbons, and so long ago as February, 1878, I laid before the Chemical Society a statement of some of the difficulties which beset this hypothesis. The formulæ which I then proposed for the terpenes I do not now pretend to sustain, inasmuch as they involve the mistaken assumption that these compounds are sexvalent, or contain three double linkings of carbon. Nevertheless, my opinion is not only unchanged, but is fortified by all that I have since learnt of these hydrocarbons, that whilst the terpenes* almost certainly contain a nucleus of six atoms of carbon, these are not disposed in the manner in which they are assumed to be in benzene, whatever constitutional formula is adopted for that substance.

The publication of a number of papers on the chemistry of the terpenes, more especially the very important researches of Wallach (*Annalen*, **225**, **227**, **230**, **238**, **239**, **241**, **245**, **246**), has attracted my attention again to the subject, and I desire to state in the first instance the grounds for my belief that the terpenes are not constituted as benzene derivatives.

The hypothesis commonly received originated in the experiments of Oppenheim, Barbier, and Kekulé, upon the production of paracymene from turpentine. C. R. A. Wright afterwards examined the action of bromine upon a number of terpenes from various sources, and found that they all gave the same cymene in different proportions. Nevertheless, the importance of this fact must not be exaggerated, for it must be remembered that the yield in the most favourable case is much below the theoretical, and cymene cannot be reconverted by any known process into a terpene. Moreover, the known hydrides of benzene, toluene, &c., are totally unlike terpenes in character. The hypothesis also accounts only for three dihydrides, assuming the propyl-group to remain the same, or six if there be a cymene con-

* Using this term to include all the liquid members of the group, natural or artificial, but not the solid "camphenes," which have totally different characters. I shall generally use Wallach's nomenclature.

taining isopropyl. The isomeric terpenes already recognised exceed this number.

A second point upon which great stress has been laid is the nature of the oxidation products of the terpenes and their derivatives, terpin hydrate, &c. As the impression seems to prevail that the terpenes when acted upon by dilute nitric acid form a productive source of paratoluic acid, I have made a few comparative experiments with the object of determining the proportion of this acid obtainable under exactly the same conditions from several terpenes, from cymene, and from paraxylene.

A weighed quantity of the hydrocarbon was in each case boiled in a flask with reflux condenser, with a quantity of nitric acid slightly in excess of that theoretically required for its oxidation to toluic acid. The nitric acid was diluted with four times its volume of water. When the hydrocarbon had disappeared, the mixture was allowed to cool, the crystallised acid filtered off, dissolved in boiling dilute solution of ammonia, then reprecipitated by dilute nitric acid, and after some hours collected, dried, and weighed. The acid thus obtained was white; it melted at about 178°, and was therefore nearly pure.

Quantities of hydrocarbon, varying from 15·9 to 17·1 grams, were taken. The following proportions are calculated from the results:—

100 parts (by weight) give of paratoluic acid—

Cymene (from turpentine)	80·1
Cymene (from cummin oil, Kahlbaum)	73·1
Paraxylene (Kahlbaum's pure)	77·2
Australene (from American turpentine)....	1·2
Terebenthene (from French turpentine)....	1·9
Hesperidene, b. p. 175° (from orange oil) ..	0

The hesperidene having failed to give any recognisable quantity of toluic acid, an experiment on a larger scale was tried. About 85 grams of the hydrocarbon gave by similar treatment an acid liquid, which when concentrated to a small bulk deposited 0·15 gram of an insoluble acid (probably terephthalic acid). The chief products of oxidation were a yellow resin, which by protracted action of strong nitric acid gave a viscid nitro-compound and oxalic acid (7·07 grams of anhydrous $H_2C_2O_4$), and a small quantity of terebic acid.

A comparison was also made between the products of oxidation by chromic acid solution upon cymene and australene, with the following result:—

Cymene, 17 grams gave 7 grams terephthalic acid, or 41 per cent.

Australene, 16·3 grams gave a trace only, insufficient to weigh, together with a minute quantity of a camphor in the condenser.

Wright (Trans., 1873, 553), in oxidising pure hesperidene by chromic acid mixture, obtained no terephthalic acid, acetic acid being the only product.

My contention has always been that the natural terpenes do not yield appreciable quantities of aromatic acids by oxidation; that they do yield by isomeric change, under the influence of heat or of reagents, compounds which must be regarded either as direct derivatives of benzene or closely connected with it, must of course be admitted. Thus not only is cymene obtainable by the removal of 2 atoms of hydrogen, but the dipentene (terpilene) obtained from the dihydrochloride got from turpentine doubtless contains a nucleus of six carbon atoms which either has assumed partly the structure of benzene, or possesses a structure which is easily transformed into that of benzene. I found that when oxidised by nitric acid, as already described, 100 parts of it gave 27·6 of toluic acid, although the turpentine from which it was derived gave practically none.

The characteristics of the terpenes as a class may be stated as follows.

The terpenes are polymerised very readily by the action of heat or of small quantities of sulphuric acid and other agents.

All the terpenes combine instantly and eagerly with chlorine and bromine, whilst benzene and cymene behave, save under exceptional circumstances, as saturated compounds.

All the terpenes unite with hydrochloric, hydrobromic, and hydriodic acids.

Some of the terpenes (the pinene-group especially) also unite slowly with the elements of water, forming two alcoholic bodies, terpineol, $C_{10}H_{17}OH$, and terpin, $C_{10}H_{18}(OH)_2$. All these characters are precisely those which are exhibited so plainly by the olefines, but in no case by hydrocarbons directly derived from benzene.

A few other facts deserve notice.

No natural terpene is recoverable from its compound with bromine or hydrochloric acid. A new hydrocarbon of the same composition, $C_{10}H_{16}$, is always formed, namely, a camphene, dipentene, terpinene, or terpinolene, according to circumstances. Again, the terpenes are resolved, when heated to a temperature of 400° to 500°, into a pentene, C_5H_8, which may be retransformed into a dipentene, $C_{10}H_{16}$, the relation between these two compounds being exactly similar to the relationship subsisting between amylene and diamylene.

If we recall the existence of the sesquiterpenes and the constituents of colophene, which are polymerides of terpene, the persistence of the

factor 5 in the number of carbon atoms, C_5H_8, $C_{10}H_{16}$, $C_{15}H_{24}$, $C_{20}H_{32}$, &c., is remarkable.

The combining capacity of the majority of the terpenes appears to be pretty definitely indicated by the formation of compounds with 2HCl, and in four cases, namely limonene (citrene), dipentene, sylvestrene, and terpinolene, with Br_4. These tetrabromides, which were all discovered by Wallach, are crystalline and stable. Nevertheless, it occurred to me as just possible that these hydrocarbons might after all possess a greater combining capacity, though the products of their combination with bromine might not be stable enough to admit of their being isolated. A new estimation of their capacity for bromine seemed also very desirable, in view of the conclusion arrived at by Gladstone (Trans., 1886, p. 609) from the refraction equivalent, and recently restated by Brühl (*Ber.*, **21**, 156), to the effect that the pinenes (australene, terebenthene, &c.), contain only one double bond, or in other words are only bivalent.

To determine the capacity for bromine, a solution of hypobromite of sodium was used. The pure hydrocarbon diluted with twice its volume of chloroform was mixed with diluted hydrochloric acid in a bottle, and the hypobromite solution added in small quantities, shaking after each addition till the hydrocarbon which settled down exhibited a faint yellowish colour. This plan being not quite satisfactory, it was found better to add at once a slight excess of the hypobromite solution, shake well for a minute, and then add some potassium iodide, and estimate by thiosulphate solution the amount of liberated iodine. Four to five grams of the hydrocarbon were taken for each experiment.

By this method, 136 parts or 1 molecule of hydrocarbon took in each case the following quantities of bromine:—

Australene (from American turpentine)	313
Terebenthene (from French turpentine)	307
Hesperidene (from orange oil)	326
Dipentene (from dihydrochloride).....	297
Calculated for Br_2 80×2	160
„ Br_4 80×4	320

There can be no doubt in these cases that the hydrocarbon fixes four atoms of bromine and no more. One molecule, or 154 parts of terpineol, $C_{10}H_{17}OH$, combined with 185·6 parts of bromine, which is only a little more than is required on the assumption that it unites with Br_2 or 160 parts. An aqueous solution of terpin, $C_{10}H_{18}(OH)_2$ does not decolorise bromine-water even after some time.

We have therefore

$C_{10}H_{16}$	$C_{10}H_{16}\begin{cases}H\\OH\end{cases}$	$C_{10}H_{16}\begin{cases}H_2\\(OH)_2\end{cases}$
Quadrivalent.	Bivalent.	Saturated.

So far the terpenes. It is well known, however, that there exists another class of compounds, the camphenes, $C_{10}H_{16}$, which are isomeric with the terpenes and derivable from them. It is unfortunate that these compounds should be so commonly classed with the terpenes, and apparently regarded by many writers as possessing a similar structure, for their chemical characteristics are very different.

When American or French turpentine oil free from water is saturated with dry hydrochloric acid gas, a solid compound is formed containing $C_{10}H_{16}HCl$. From this the elements of hydrochloric acid may be withdrawn, though with difficulty, by the action of alcoholic potash or of sodium acetate, &c. The resulting hydrocarbon is camphene, optically active or inactive according to circumstances. It is a solid, melting at 48°, and boiling at 160°. The same substance is formed in considerable quantity among the products of the action of strong sulphuric acid upon turpentine (Armstrong and Tilden, Trans., 1879, 733). It is also formed by the action of sodium upon the hydrochloride, $C_{10}H_{16}HCl$, from turpentine, and is obtainable through the chloride from borneol, and hence from camphor.

Camphene differs notably from the terpenes in its chief product of oxidation, for it yields neither toluic nor terephthalic acid, but acetic acid and camphor. It does not combine with bromine, but forms an ill-defined liquid monobromo-compound, $C_{10}H_{15}Br$ (Wallach, *Ann.*, **230**, 235).

It does unite with 1 mol. of hydrochloric acid, forming a compound which is very similar in appearance to the monohydrochloride, $C_{10}H_{16}HCl$, prepared from turpentine oil, but differs from that compound in dissociating into a hydrocarbon and HCl when heated (Ehrhardt, *Chem. News*, **54**, 239), and in yielding up readily the elements of HCl when boiled with water or alkaline solutions, regenerating the camphene.

There are three varieties of this hydrocarbon, which agree completely in all physical and chemical characters, except in their action on polarised light, the one possessing right-handed rotatory power, another being left-handed, whilst the third is inactive.

When turpentine unites with dry hydrochloric acid, therefore, a change is induced manifestly more profound than that which occurs when it combines with 2HCl, as it does in the presence of water or alcohol. This latter compound when heated alone or with aniline readily yields liquid dipentene, which in general characters is very similar to the original hydrocarbon, and is probably identical with the optically inactive product of the action of heat upon turpentine.

We must therefore recognise the following chemically distinct isomerides (see also Wallach, *Ann.*, **239**, 45).

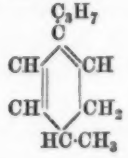
I. Natural Terpenes (optically active liquids).
   1. Pinene (australene and terebenthene).
   2. Limonene (citrene).
   3. Sylvestrene (from Swedish turpentine).
   4. Phellandrene (from *Phellandrium aquaticum*, &c., Pesci, *Gazz. Chim.*, **16**, 225).

II. Artificial Terpenes (optically inactive liquids).
   1. Dipentene (from the dihydrochloride, $C_{10}H_{16}2HCl$, m. p. 48°).
   2. Terpinolene (from the action of sulphuric acid on terpin).
   3. Terpinene („ „ „).

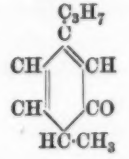
III. Artificial Camphenes (solids—two optically active in opposite directions—one inactive).

The combining capacity of none of these exceeds four units. Consequently it is not possible to represent the nucleus of six carbon-atoms, which undoubtedly they all contain, as forming an open chain. They must be united into a closed chain containing at the most two double bonds. Hence we are driven to such formulæ as those which have been proposed by Oppenheim (*Ber.*, **5**, 98), by Goldschmidt and Zürrer (*Ber.*, **18**, 1729, and **20**, 486), by Wallach (*Annalen*, **239**, 46), and more recently by Brühl (*Ber.*, **21**, 165). Goldschmidt and Zürrer derive the formula of limonene (= carvene or citrene) from that of carvol, in consequence of the relations which they have established between these two compounds. Thus:—

Limonene.



Carvol.

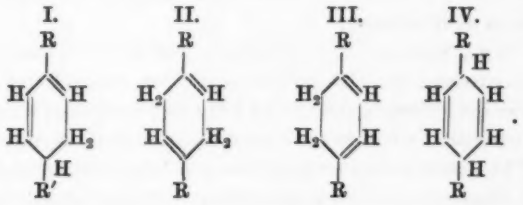


Unfortunately the constitution of carvol as a benzene-derivative is not fully established, for its conversion into carvacrol is attended by a very energetic reaction, in the course of which we may well believe that a profound alteration of structure occurs.

Wallach has shown in a very plausible way how the polymerisation of isoprene, C_5H_8 (assumed to be $CH_2{:}C(CH_3){\cdot}CH{:}CH_2$) into dipentene may be accounted for by a similar formula. I do not agree with him in some points of detail, for example, in his statement that pinenes contain only one double bond, for, as shown on a previous page, the pinenes combine with the same amount of bromine as the citrenes, and they form with hydrochloric acid the same dihy-

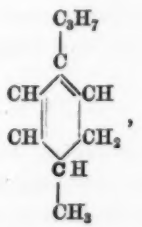
drochloride. Neither can I accept his formula for solid camphene, which certainly contains no double bond at all, as testified by its indifference to bromine. But I am glad to observe that he adopts the view which I have so long maintained, that pinene (turpentine oil "kein gewöhnliches Hydrocymol ist" (*Ann.*, **239**, 48).

The formulæ for the terpenes range themselves under several types, which represent them all as containing two double bonds, such as are conveniently called ethylenic bonds. The most probable of these are represented as follows, in which R and R′ stand for the two groups methyl and propyl.



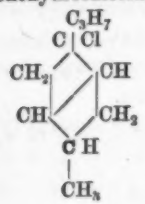
Of course others may be conceived, as, for example, by exchange of position by R and R′ in I.

At present, however, we do not know whether all the different species have yet been recognised. There may be other isomerides which must hereafter be taken into account, and there is very little to guide us in assigning to each known hydrocarbon its appropriate formula. It will be sufficient, therefore, if I indicate the manner in which they may be used by reference to one example. Adopting a formula of type I for turpentine—

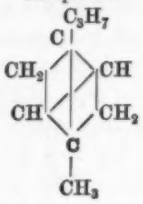


and indicating the asymmetric atom of carbon which it contains by a black-faced letter, its transformation into the monohydrochloride, and this subsequently into camphene and camphor, may be represented by the following formulæ:—

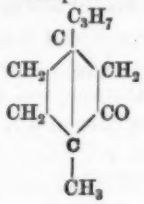
Terpene monohydrochloride.



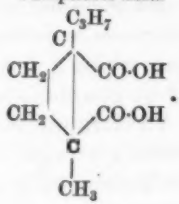
Camphene.



Camphor.



Camphoric acid.



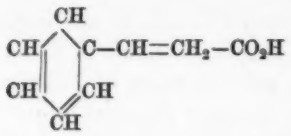
But it will naturally be remarked that such formulæ as these, which have been proposed for the terpenes, are the accepted formulæ for derivatives of benzene.

Oppenheim's formula for turpentine, which is identical with that given above, except that the positions of the methyl and propyl are reversed, was deliberately contrived for the purpose of exhibiting the relation of turpentine to benzene as indicated by its conversion into cymene. The conclusion to which we are impelled is that Kekulé's formula for benzene must be abandoned. If the evidence for this conclusion rested solely upon our present imperfect knowledge of the terpenes it would of course possess but little value. This, however, is not the case.

The chief objection which has been raised against Kekulé's formula, namely, that the positions 1 : 2 and 1 : 6 are not identical, has been met by a well-known hypothesis due to Kekulé himself. That hypothesis has very little probability in its favour, but whether that explanation is now generally accepted is not of great importance in the presence of another objection which has not been so generally recognised as I think it deserves to be. Kekulé's formula represents benzene as containing three times over the same kind of linking of the carbon atoms which we must admit in the case of ethylene, viz.:—

$$—C{=}C—.$$

It is characteristic of this grouping that it is associated with the capacity for instantaneous combination with bromine, with the hydracids, &c. In benzene we have a compound which exhibits no trace of this character. Bromine dissolves in benzene without forming addition products after the manner of the olefines and other hydrocarbons, in which we assume the existence of double or treble linking, and only under exceptional circumstances are these addition products formed. In the formulæ of many aromatic compounds the same symbol is used to represent two distinct functions. Thus in cinnamic acid, for example—



the atoms of carbon united by two bonds in the side-chain combine instantly with HBr or HI, with Br_2 or with HClO. They are in fact strictly ethylenic in character. The two double bonds in the hexagon correspond to nothing of the kind, for they do not unite in the same way under similar circumstances. Doubtless most chemists have been in the habit of indulging in a mental reservation as to the significance of the double bond in a closed chain. This, however, does not justify the employment of the same symbol to express two different things.

Again, when benzene and its homologues are submitted to oxidation, the six carbon atoms remain very persistently united, and a series of acids containing a nucleus of C_6 results. In other cases where double linking unquestionably occurs, it seems very often to be a point of weakness, the carbon atoms thus united separating more readily than those which are united by single bonds. Allyl alcohol, for example, gives by the action of dilute nitric acid, formic (or carbonic) and oxalic acids. Now this splitting up of the double bonds in a formula like that which Kekulé attributed to benzene ought to yield abundance of oxalic acid. This is what the terpenes do, but which benzene and its homologues do not.

v. Baeyer, in some important papers (*Ber.*, **19**, 1797, and more recently *Annalen*, **245**, 103), describes the remarkable properties of the hydroterephthalic acids, and points out that these compounds no longer possess the character of benzene derivatives, but in spite of the ring-like arrangement of the carbon atoms, their chemical nature indicates that they must be regarded as compounds of the fatty series. There is in fact the same sort of relation between the properties of terephthalic acid and dihydroterephthalic acid that there is between cymene and the terpenes.

In order to explain the peculiarities of the hydroterephthalic acids, v. Baeyer proposes a theory which seems to be nearly identical with that enunciated by Armstrong about a year previously (*Phil. Mag.*, Feb., 1887). In benzene and its immediate derivatives he assumes that the six carbon atoms form a symmetrical figure. One unit of valency of each draws the carbon atoms towards the centre of the ring, but v. Baeyer expressly states that they must not be assumed to be free in the ordinary sense, neither are opposite carbons united together, the central units of valency are only to be regarded as passive. It seems to me, as already pointed out by Ladenburg

(*Annalen*, **246**, 382), very difficult, if not impossible, to distinguish this formula from the diagonal formula of Claus.

I do not think the present state of knowledge in regard to this matter enables us to state more than the following propositions:—

1. The six atoms of carbon in benzene form a very stable group, which is not easily broken up by heat or by chemical agents.

2. The carbon atoms are all in the same condition, and the hydrogen is distributed equally among them.

3. The carbon atoms are not united together by ethylenic bonds.

4. There are three, and only three, disubstitution-derivatives.

Either of the formulæ of Claus, of v. Baeyer, of Armstrong, or the prism of Ladenburg satisfies these conditions, but at present there seems no solid reason for preferring one before the other. With regard to the Claus formula, v. Baeyer has already pointed out that in any ring-like arrangement the carbons in the *para*-position must be further apart than those in the *ortho*-position, and hence the existence of three isomeric diderivatives may be accounted for.

Brühl's two recent papers on the terpenes and their derivatives (*Ber.*, **21**) contain suggestions as to the constitution of the terpenes, based upon the observation of their refraction equivalents. These papers have been already very severely criticised by Wallach (*Annalen*, **245**, 121), and I need only add that I agree with the latter in thinking that much reliance cannot be placed upon the recorded values of the refraction equivalents in this group of compounds, by reason of the more than doubtful purity of many of the substances operated upon. And when the conclusions are in direct conflict with those derived from the most obvious chemical properties, as, for example, when the saturating power of camphene, which is untouched by bromine, is represented as being the same as that of terebenthene, which instantly combines with four atoms of bromine, all we can do is to wait for further information as to their optical properties and the relation in which these stand to chemical constitution.

Evidence from other sources, so far as it is available, supports the view that I have adopted. Thus Hartley (*Proc. Roy. Soc.*, 1879, **29**, 290) found that australene, terebenthene, and hesperidene gave none of the bands which are exhibited in the spectrum of the ultra-violet by cymene and other undoubted benzenoid compounds. And from Abney and Festing's (*Phil. Trans.*, 1881) observations at the opposite extremity of the spectrum, the crucial line 867, with its attendant band characteristic of benzene-derivatives, is not seen in the absorption-spectrum of turpentine.

LXXV.—*Combustion by Means of Chromic Anhydride.*

By C. F. Cross and E. J. Bevan.

Some time since we published a preliminary note of results obtained on the combustion of carbohydrates with chromic anhydride and sulphuric acid as a method of ultimate analysis (*Chem. News*, October 23, 1885). Having observed that carbonic oxide was formed and evolved with the carbonic anhydride, we found it necessary to abandon gravimetric methods and to measure the volume of the evolved gas, the proportion of carbon per unit of *volume* being independent of the ratio CO : CO_2. We have employed mercury as the confining liquid, and an apparatus consisting of a U-tube graduated in the one limb which is in connection with the combustion flask, the other limb being open to the air, and connected with a reservoir of mercury, by means of which the levels are adjusted for reading (*Rep. Anal. Chem.*, 1887, 37). In some cases, we have employed a Lunge's nitrometer, but the particular form of apparatus to be employed for the purpose is rather a matter of detail.

Before proceeding to deal with the results obtained, we must briefly notice a well-known paper of Ladenburg's, published in 1865 (*Annalen*, **135**, 1), on the subject of ultimate analysis by the few methods other than incandescent combustion which are available. In this paper, we find chromic acid mentioned, but dismissed as unavailable by reason of its decomposition on heating with sulphuric acid, with evolution of oxygen. This decomposition was specially studied by one of us (Cross and Higgin, Trans., 1882, 113), with the result of showing that it took place only at high temperatures, the evolution of oxygen being imperceptible up to a temperature some degrees above 100°, and becoming brisk only as the boiling point of the acid was reached. At the same time it was noticed that the course of the decomposition differed somewhat when potassium dichromate was substituted for the chromic anhydride, taking place more readily, and yielding a sulphate of different character and composition. Ladenburg having dismissed chromic acid apparently as a result of a general impression of its instability, finally selected iodic acid, added in the form of silver iodate to the sulphuric acid used as the liquid auxiliary. His combustions were performed with this mixture in sealed tubes, and his estimations consisted in determining the loss of weight after completely removing the gaseous products, and the total oxygen consumed. The results he obtained leave nothing to be desired in point of accuracy, and we can only conclude that it is the trouble and

risk attending operations with sealed tubes which have deterred chemists from adopting this method.

On the other hand, with an open combustion such as that we have employed, the operation is a very simple one, completed in a few minutes, and if proved to be accurate would be a useful addition to our laboratory methods, even if its applications were limited. But apart from any question of application, the results of such combustions, partial for certain groups of compounds, complete in others, cannot fail to throw some light on the problems of the molecular constitution of carbon compounds. We shall, therefore, in the meantime content ourselves with recording the results obtained, and leave it to the progress of research to determine their value.

The proportion of carbonic oxide formed in the combustion of the carbohydrates depends very much upon the conditions of the decomposition. We have found, under those which we have perhaps arbitrarily selected, that it is reduced to a minimum; this being so, and a strict uniformity in the conditions being observed, the "error of the apparatus" we find satisfactorily constant. The conditions we may note here are:—(1) A quantity of substance to be used yielding from 90 to 100 c.c. of gas; (2) the same volume of sulphuric acid, namely, 9 c.c., must be employed; (3) an excess of chromic acid of about 30 per cent. beyond that required for complete combustion.

The substance, cellulose for example, being dissolved in the acid, and the chromic anhydride introduced in a small tube into the neck of the flask, the latter is connected in the horizontal position with the U-tube, and after a suitable interval the level of the mercury is brought to zero. The thermometer having been read off, the tube containing the chromic anhydride is allowed to fall to the bottom of the flask, and is well shaken with the acid solution. The combustion proceeds rapidly, the temperature rising to 60—70°; after about two-thirds of the gas has been collected, it is necessary to apply heat, the remainder of the gas being rapidly expelled at 100°. The conclusion of the combustion is well marked by the cessation of the frothing which accompanies the evolution of the gas in the viscous medium. The flask is allowed to cool, and the gas volume read off with the usual precautions. If again heated, and a second reading taken after cooling, it will be found identical with the first. We may take this, together with the numerical results about to be described, as sufficient evidence of the stability of the chromic anhydride under the conditions of the combustion. But we shall revert subsequently and more specifically to this point.

In order to "standardise" the apparatus, and to determine the error due to the absorption of carbonic acid, we made several series of combustions of oxalic acid. We may cite the results of one of these,

consisting of 16 experiments. The weight of substance taken varied from 0·05 gram to 0·25 gram. The mean percentage of carbon calculated from the gas volume obtained was 26·0 ($C_2H_2O_4 = 26·6$), with a probable error for a single observation of $\pm$ 0·2 per cent.

The absorption of CO_2 by H_2SO_4 is 0·75 vol. at ordinary temperatures. After reading off, and allowing an interval of some minutes before taking a second reading, we found that the latter showed no perceptible difference. But after half an hour a difference of level was manifest; in two hours the diminution of volume amounted to from 3—5 c.c. This is no doubt attributable to a gradual absorption of the gas by the acid. The absorption, therefore, under the conditions of observation adopted, is only a fraction of the theoretical maximum, and, as we find, about 2/7. Supposing this absorption constant, and the quantity of substance weighed for combustion to

	Weight taken.	Gas volume corrected to 0° and 760 mm.	Percentage carbon.	
			Found.*	Calculated.
Cellulose.				
Swedish filter-paper ..	0·1150	94·6 c.c.	44·0	44·4
	0·1157	94·1 „	43·6	—
	0·1165	94·5 „	43·4	—
	0·1141	93·5 „	43·9	—
	0·1143	94·0 „	44·0	—
	0·1147	94·9 „	44·3	—
	0·1280	104·3 „	43·6	—
Oxalic Acid.....	0·1344	66·1 „	26·3	26·6
	0·1305	64·0 „	26·2	—
	0·1750	86·2 „	26·3	—
	0·2080	102·2 „	26·2	—
	0·2020	98·0 „	26·0	—
Citric Acid.....	0·1625	108·9 „	35·9	37·5
Glycerin.....	0·1337	92·6 „	37·1	37·5
Phthalic Acid.....	0·0962	101·5 „	56·6	57·8
Salicylic Acid.....	0·0966	108·6 „	60·2	60·8
	0·0945	104·8 „	59·4	—
Phthalic Anhydride ..	0·0881	105·0 „	63·8	64·8
	0·0922	109·0 „	63·8	—
Benzoic Acid	0·0895	113·1 „	67·8	68·8
	0·0850	107·5 „	67·8	—

* The correction to be applied to these calculated numbers will be dealt with subsequently.

vary, the error, in defect, should vary in inverse proportion. We found the evidences of such a variation in our numbers, but the proportion was not sufficiently strict to be made the basis of a correction. We therefore found it necessary to eliminate the variation of the gas volume. Keeping this within the limits of 80—110 c.c., and comparing substances of varying carbon percentage, we find that the error is, with sufficient approximation, directly proportioned to the carbon percentage.

We give a selection of results (p. 891), obtained in series, showing the degree of approximation attainable in combustion according to this method.

A very large number of our earlier determinations were made with quantities of substance yielding gas volumes varying from 50—120 c.c. We do not think it necessary to reproduce these, since they merely serve to indicate the conditions necessary to secure a constant error. Under these conditions, already defined, the error may be empirically expressed by the following fraction:

$$\frac{\text{Carbon percentage of substance}}{25} \times 0{\cdot}4,$$

that is, the percentage calculated from the gas volume must be increased by this amount to give the true percentage. In order to investigate the process from the point of view of the oxidising substance, the following combustions of cellulose, purified bleached cotton, were carried out under the above conditions, but with a weighed quantity of potassium dichromate in excess. The residual chromic acid was determined by titration with ferrous sulphate in the usual way. The chromic acid used is expressed as the equivalent of oxygen; the quantity necessary for complete combustion to CO_2 is given side by side for comparison:—

Weight of cellulose.	Oxygen consumed.	Oxygen to burn to CO_2.	CO : CO_2.
0·1805	0·2010	0·2107	0·0169 : 0·2630
0·1803	0·2060	0·2106	0·0080 : 0·2770
0·1940	0·2126	0·2297	0·0294 : 0·2825
(*a*.) 0·1164	0·1350	0·1387	0·0065 : 0·1805
(*b*.) 0·1120	0·1300	0·1325	0·0044 : 0·1753

In the two latter the combustion was carried out in connection with the gas collecting apparatus; the following were the volumes estimated, corrected to 0° and 760 mm.

(*a*.) 94·5 = 43·5 C per cent.
(*b*.) 91·4 = 43·6 „

Taking the mean of these we may apply the correction as above described:—

$$43{\cdot}55 + \frac{43{\cdot}55}{25} \times 0{\cdot}4 = 44{\cdot}25 \text{ per cent. carbon.}$$

These numbers indicate a complete combustion to gaseous products, in which the proportion of carbonic oxide is very small. The formation of carbonic oxide we had verified at the time of publishing our first communication, by finding a combustible gas, burning with the characteristic blue flame, left after absorbing the carbonic acid by potash; the quantity of cellulose treated for the purpose being sufficient to yield 500 c.c. of gas. We have since made two observations on the gases evolved, (*a*) in the earlier stages, (*b*) in the latter stages of the combustion, under the conditions obtaining in our quantitative experiments:—

(*a*.) 40·5 c.c. treated with Cu_2Cl_2 in HCl gave a contraction of 2·5 c.c.

(*b*.) 30·8 c.c. treated with KOH gave a contraction of 30·4 c.c.

The corresponding ratio by *weight* are (*a*) CO. CO_2. 1 : 24 (*b*) CO. CO_2. 1 : 117.

The proportion of CO, therefore, varies with the conditions of the combustion.

We have now briefly to notice those cases in which our investigations have shown that the combustion is partial, these are more particularly acids of the fatty series and compounds containing nitrogen.

Combustions of palmitic and stearic acids with chromic anhydride yielded from 60—70 per cent. carbon in the form of gaseous products, and the results are variable. The partial nature of the combustion is referable to molecular structure rather than to the relatively large proportion of carbon, for we have obtained good results with aromatic compounds containing as much as 90 per cent. of carbon.

The second group of compounds which only partially burns is that of the organic bases. We propose to investigate this subject further: it is probable that useful information will be gained by a study of the residual products of combustion. It is worthy of note that under the conditions we have described, urea is not attacked.

In the course of this research we have made a number of observations on the behaviour of chromic anhydride and potassium dichromate when heated with sulphuric acid. We may cite the following:—

(*a*.) 0·010 gram CrO_3, heated at 100° with 9 c.c. sulphuric acid for three hours. No appreciable reduction.

(*b.*) 0·500 CrO_3, heated with 9 c.c. H_2SO_4 at 100° one hour, flask connected to gas apparatus. Increase of vol. at 16° (corr.) 0·75 c.c.

(*c.*) 0·300 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°; residual $K_2Cr_2O_7$—estimated with $FeSO_4$—0·286; 0·014 decomposed in two hours. Eqt. of O evolved 0·0023.

(*d.*) 0·590 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°. Residual $K_2Cr_2O_7$ determined 0·5700. 0·020 decomposed.

(*e.*) 1·574 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°. Cr_2O_3 formed 0·101.

(*f.*) 1·904 CrO_2, heated with 9 c.c. H_2SO_4 two hours at 105°. Cr_2O_3 formed 0·085.

These results are sufficient to show that the instability* of the chromic anhydride begins to be manifest at 105°; the decomposition however, even at this temperature is extremely slow. It is more rapid with the dichromate than the anhydride, and, in both cases, increases with the mass.

The explanation of this we take to be that the portion remaining undissolved is more liable to decomposition than that dissolved in the acid. It is to be observed, however, that the conditions in the blank experiments above cited differ from those in the combustion process, by the absence of the sesquioxide and the presence of a large proportion of undissolved trioxide. The sesquioxide is peroxidised by the trioxide, as is well known, and its presence therefore is an additional element of stability. Finding no mention of investigations of the oxidation of the sesquioxide in presence of sulphuric acid, we made observations on this point. We find that it is rapidly oxidised to the trioxide by permanganate, under this condition; also, though less rapidly, by manganese dioxide.

The comparative stability of the trioxide under the conditions of the combustion is probably therefore due in part to the presence of the sesquioxide, as also to the relatively small mass of residual trioxide, and its being dissolved in the acid solution.

We made observations on the stability of the acid mixture which remained at the conclusion of a combustion of 0·14 gram of cellulose.

(*g.*) The combustion having been finished by raising the temperature to 90°, and agitating until no more frothing appeared, the acid solution (9 c.c.) was sealed in a tube of 20 c.c. capacity. This was heated at 104° for 1 hour. The tube, after cooling, was opened in gas-tight connection with a U-tube of mercury. A difference of level of 6 mm. was observed. The total volume

* The anhydride heated by itself begins to decompose at 250°.

between the sulphuric acid in the tube and the mercury in the U-tube being 30 c.c., the increase of gas in the tube is 0·3 c.c. at 15°.

(*h.*) The tube was again sealed and heated for two hours at 100°. The difference of level in the U-tube on opening it, after cooling, was 40 mm.; the corresponding increase of volume in the tube 1·6 c.c.

(*i.*) Again sealed and heated for two hours at 190°, the gas evolved in the tube amounted to 2·3 c.c.

(*j.*) A similar mixture of sulphuric acid, chromic sulphate, and chromic anhydride was heated in a flask connected with a gas apparatus, as in a combustion, for 1½ hours at 105°. The increase of volume was 3 c.c.

These experiments are sufficient to show that the error due to decomposition of the chromic anhydride during the comparatively short period of heating necessary to complete the combustion, is so small that it may be neglected.

We wish to express our thanks to our friends, Mr. R. Merriman, for his assistance in the research, and to Mr. A. Green for kindly supplying pure preparations for analysis.

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Page	Line		
749	20 from bottom,	*for*	"hulled" *read* "unhulled."

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119	13	„	„	"$-758{\cdot}97p$" *read* "$+758{\cdot}97p$."
125	top line		„	"p" „ "p_1."
476	8 from	„	„	"H. H. MacMunns" *read* "H. H. McMinnies."
723	top line		„	"triethylbenzoylphosphonium" *read* "triethylbenzylphosphonium."
782	12 from top		„	"Dr. Tilden" *read* "Tilden and Shenstone."
814	13	„	„ *insert*	"Chlorides of" *before* "Indium."

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